7. Master Equations and Jump Processes

It is very often the case that in systems involving numbers of particles, or individual objects (animals, bacteria, etc) that a description in terms of a jump process can be very plausibly made. In such cases we find, as first mentioned in Sect. 1.1, that in an appropriate limit *macroscopic deterministic* laws of motion arise, about which the random nature of the process generates a fluctuating part. However the deterministic motion and the fluctuations arise directly out of the same description in terms of individual jumps, or transitions. In this respect, a description in terms of a jump process (and its corresponding master equation) is very satisfactory.

In contrast, we could model such a system approximately in terms of stochastic differential equations, in which the deterministic motion and the fluctuations have a completely independent origin. In such a model this independent description of fluctuations and deterministic motion is an embarrassment, and fluctuation dissipation arguments are necessary to obtain some information about the fluctuations. In this respect the master equation approach is a much more complete description.

However the existence of the macroscopic deterministic laws is a very significant result, and we will show in this chapter that there is often a limit in which the solution of a master equation can be approximated asymptotically (in terms of a large parameter Ω describing the system size) by a deterministic part (which is the solution of a deterministic differential equation), plus a fluctuating part, describable by a stochastic differential equation, whose coefficients are given by the original master equation. Such asymptotic expansions have already been noted in Sect. 3.8.3, when we dealt with the Poisson process, a very simple jump process, and are dealt with in detail in Sect. 7.2.

The result of these expansions is the development of rather simple rules for writing Fokker-Planck equations equivalent (in an asymptotic approximation) to master equations, and in fact it is often in practice quite simple to write down the appropriate approximate Fokker-Planck equation without ever formulating the master equation itself. There are several different ways of formulating the first-order approximate Fokker-Planck equation, all of which are equivalent. However, there is as yet only one way of systematically expanding in powers of Ω^{-1}, and that is the system size expansion of van Kampen.

The chapter concludes with an outline of the *Poisson representation*, a method devised by the author and co-workers, which, for a class of master equations, sets up a Fokker-Planck equation *exactly* equivalent to the master equation. In this special case, the system size expansion arises as a small noise expansion of the Poisson representation Fokker-Planck equation.

7.1 Birth-Death Master Equations—One Variable

The one dimensional prototype of all birth-death systems consists of a population of individuals X in which the number that can occur is called x, which is a non-negative integer. We are led to consider the conditional probability $P(x, t\,|\,x', t')$ and its corresponding master equation. The concept of birth and death is usually that *only a finite number of X are created (born) or destroyed (die) in a given event.* The simplest case is when the X are born or die one at a time, with a time independent probability so that the transition probabilities $W(x\,|\,x', t)$ can be written

$$W(x\,|\,x', t) = t^+(x')\delta_{x,x'+1} + t^-(x')\delta_{x,x'-1}\,. \tag{7.1.1}$$

Thus there are two processes,

$$x \rightarrow x+1: \qquad t^+(x) = \text{transition probability per unit time.} \tag{7.1.2}$$

$$x \rightarrow x-1: \qquad t^-(x) = \text{transition probability per unit time.} \tag{7.1.3}$$

The general master equation (3.5.5) then takes the form

$$\begin{aligned}\partial_t P(x, t\,|\,x', t') = {} & t^+(x-1)P(x-1, t\,|\,x', t') + t^-(x+1)P(x+1, t\,|\,x', t') \\ & - [t^+(x) + t^-(x)]P(x, t\,|\,x', t')\,.\end{aligned} \tag{7.1.4}$$

There are no general methods of solving this equation, except in the time-independent situation.

7.1.1 Stationary Solutions

We can write the equation for the stationary solution $P_s(x)$ as

$$0 = J(x+1) - J(x) \tag{7.1.5}$$

with

$$J(x) = t^-(x)P_s(x) - t^+(x-1)P_s(x-1)\,. \tag{7.1.6}$$

We now take note of the fact that x is a non-negative integer; we cannot have a negative number of individuals. This requires

$$\text{(i)}\ t^-(0) = 0: \qquad \text{no probability of an individual dying if there are none present;} \tag{7.1.7}$$

$$\text{(ii)}\ P(x, t\,|\,x', t') = 0 \qquad \text{for } x < 0 \text{ or } x' < 0\,. \tag{7.1.8}$$

This means that

$$J(0) = t^-(0)P_s(0) - t^+(-1)P_s(-1) = 0\,. \tag{7.1.9}$$

We now sum (7.1.5) so

$$0 = \sum_{z=0}^{x-1} [J(z+1) - J(z)] = J(x) - J(0)\,. \tag{7.1.10}$$

Hence,

$$J(x) = 0 \tag{7.1.11}$$

and thus

$$P_s(x) = \frac{t^+(x-1)}{t^-(x)} P_s(x-1) \tag{7.1.12}$$

so that

$$\boxed{P_s(x) = P_s(0) \prod_{z=1}^{x} \frac{t^+(z-1)}{t^-(z)}\,.} \tag{7.1.13}$$

a) Detailed Balance Interpretation

The condition $J(x) = 0$ can be viewed as a *detailed balance requirement*, in which x is an even variable. For, it is clear that it is a form of the detailed balance condition (5.3.74), which takes the form here of

$$P(x, \tau | x', 0) P_s(x') = P(x', \tau | x, 0) P_s(x)\,, \tag{7.1.14}$$

Setting $x' = x \pm 1$ and taking the limit $\tau \to 0$, and noting that by definition (3.4.1),

$$W(x | x', t) = \lim_{\tau \to 0} P(x, t + \tau | x', t)/\tau\,, \tag{7.1.15}$$

the necessity of this condition is easily proved.

b) Rate Equations

We notice that the mean of x satisfies

$$\partial_t \langle x(t) \rangle = \partial_t \sum_{x=0}^{\infty} x P(x, t | x', t') \tag{7.1.16}$$

$$= \sum_{x=0}^{\infty} x[t^+(x-1) P(x-1, t | x', t') - t^+(x) P(x, t | x', t')]$$

$$+ \sum_{x=0}^{\infty} x[t^-(x+1) P(x+1, t | x', t') - t^-(x) P(x, t | x', t')] \tag{7.1.17}$$

$$= \sum_{x=0}^{\infty} [(x+1) t^+(x) - x t^+(x) + (x-1) t^-(x)$$

$$- x t^-(x)] P(x, t | x', t')\,, \tag{7.1.18}$$

i.e.,

$$\boxed{\frac{d}{dt} \langle x(t) \rangle = \langle t^+[x(t)] \rangle - \langle t^-[x(t)] \rangle\,.} \tag{7.1.19}$$

The corresponding deterministic equation is that which would be obtained by neglecting fluctuations, i.e.,

$$\frac{dx}{dt} = t^+(x) - t^-(x)\,. \tag{7.1.20}$$

Notice that a stationary state occurs deterministically when

$$t^+(x) = t^-(x)\,. \tag{7.1.21}$$

Corresponding to this, notice that the maximum value of $P_s(x)$ occurs when

$$P_s(x)/P_s(x-1) \simeq 1\,, \tag{7.1.22}$$

which from (7.1.12) corresponds to

$$t^+(x-1) = t^-(x)\,. \tag{7.1.23}$$

Since the variable x takes on only integral values, for sufficiently large x (7.1.21) and (7.1.23) are essentially the same.

Thus, the *modal value of* x, which corresponds to (7.1.23), is the stationary stochastic analogue of the deterministic steady state which corresponds to (7.1.21).

7.1.2 Example: Chemical Reaction $X \rightleftharpoons A$

We treat the case of a reaction $X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A$ in which it is assumed that A is a fixed concentration. Thus, we assume

$$t^+(x) = k_2 a \tag{7.1.24}$$

$$t^-(x) = k_1 x \tag{7.1.25}$$

so that the Master equation takes the simple form [in which we abbreviate $P(x, t | x', t')$ to $P(x, t)$]

$$\partial_t P(x, t) = k_2 a P(x-1, t) + k_1 (x+1) P(x+1, t) - (k_1 x + k_2 a) P(x, t). \tag{7.1.26}$$

a) Generating Function

To solve the equation, we introduce the generating function (c.f. Sects.1.4.1, 3.8.2)

$$G(s, t) = \sum_{x=0}^{\infty} s^x P(x, t) \tag{7.1.27}$$

so that

$$\boxed{\partial_t G(s, t) = k_2 a (s-1) G(s, t) - k_1 (s-1) \partial_s G(s, t)\,.} \tag{7.1.28}$$

If we substitute

$$\phi(s, t) = G(s, t) \exp(-k_2 as/k_1)\,, \tag{7.1.29}$$

(7.1.28) becomes

$$\partial_t \phi(s, t) = -k_1(s-1)\partial_s \phi(s, t)\,. \tag{7.1.30}$$

The further substitution $s - 1 = e^z$,

$$\phi(s, t) = \psi(z, t)$$

gives

$$\partial_t \psi(z, t) + k_1 \partial_z \psi(z, t) = 0 \qquad (7.1.31$$

whose solution is an arbitrary function of $k_1 t - z$. For convenience, write this a

$$\begin{aligned}\psi(z, t) &= F[\exp(-k_1 t + z)]\, e^{-k_2 a/k_1} \\ &= F[(s-1)e^{-k_1 t}]\, e^{-k_2 a/k_1}\end{aligned}$$

so

$$\boxed{G(s, t) = F[(s-1)e^{-k_1 t}] \exp[(s-1)k_2 a/k_1]\,.} \qquad (7.1.3$$

Normalisation requires $G(1, t) = 1$, and hence

$$F(0) = 1\,. \tag{7.1.33}$$

b) Conditional Probability

The initial condition determines F; this is (setting $t' = 0$)

$$P(x, 0 \mid N, 0) = \delta_{x,N} \tag{7.1.34}$$

which means

$$G(s, 0) = s^N = F(s-1) \exp[(s-1)k_2 a/k_1] \tag{7.1.35}$$

so that

$$G(s, t) = \exp\left[\frac{k_2 a}{k_1}(s-1)(1 - e^{-k_1 t})\right][1 + (s-1)\,e^{-k_1 t}]^N\,. \tag{7.1.36}$$

This can now be expanded in a power series in s giving

$$\boxed{\begin{aligned}P(x, t \mid N, 0) = \exp\left[-\frac{k_2 a}{k_1}(1 - e^{-k_1 t})\right] \sum_{r=0}^{x} \frac{N!}{(N-r)!\,r!\,(x-r)!}\left(\frac{k_2 a}{k_1}\right)^{x-r} \\ \times (1 - e^{-k_1 t})^{N+x-2r} e^{-k_1 t r}\,.\end{aligned}} \tag{7.1.37}$$

This very complicated answer is a complete solution to the problem but is of very little practical use. It is better to work either directly from (7.1.36), the generating function, or from the equations for mean values.

From the generating function we can compute

$$\boxed{\begin{aligned}
&\langle x(t)\rangle &&= \partial_s G(s=1, t) = \frac{k_2 a}{k_1}(1 - e^{-k_1 t}) + N\,e^{-k_1 t} &&(7.1.38)\\
&\langle x(t)[x(t)-1]\rangle &&= \partial_s^2 G(s=1, t) = \langle x(t)\rangle^2 - N\,e^{-2k_1 t} &&(7.1.39)\\
&\operatorname{var}\{x(t)\} &&= \left(N\,e^{-k_1 t} + \frac{k_2 a}{k_1}\right)(1 - e^{-k_1 t})\,. &&(7.1.40)
\end{aligned}}$$

c) Moment Equations

From the differential equation (7.1.28) we have

$$\partial_t[\partial_s^n G(s, t)] = \{n[k_2 a \partial_s^{n-1} - k_1 \partial_s^n] + (s-1)[k_2 a \partial_s^n - k_1 \partial_s^{n+1}]\}\, G(s, t)\,. \tag{7.1.41}$$

Setting $s = 1$ and using

$$\partial_s^n G(s, t)|_{s=1} = \langle x(t)^n \rangle_f\,, \tag{7.1.42}$$

we find

$$\boxed{\frac{d}{dt}\langle x(t)^n \rangle_f = n[k_2 a \langle x(t)^{n-1} \rangle_f - k_1 \langle x(t)^n \rangle_f]} \tag{7.1.43}$$

and these equations form a closed hierarchy. Naturally, the mean and variance solutions correspond to (7.1.38, 40).

d) Autocorrelation Function and Stationary Distribution

As $t \to \infty$ for any F, we find from (7.1.32, 33)

$$G(s, t \to \infty) = \exp[(s-1)k_2 a/k_1] \tag{7.1.44}$$

corresponding to the *Poissonian solution:*

$$P_s(x) = \exp(-k_2 a/k_1)\,(k_2 a/k_1)^x/x!. \tag{7.1.45}$$

Since the equation of time evolution for $\langle x(t)\rangle$ is *linear*, we can apply the methods of Sect.3.7.4, namely, the regression theorem, which states that the stationary autocorrelation function has the same time dependence as the mean, and its value at $t = 0$ is the stationary variance. Hence,

$$\boxed{\begin{aligned}
&\langle x(t)\rangle_s &&= k_2 a/k_1 &&(7.1.46)\\
&\operatorname{var}\{x(t)\}_s &&= k_2 a/k_1 &&(7.1.47)\\
&\langle x(t), x(0)\rangle_s &&= e^{-k_1 t} k_2 a/k_1\,. &&(7.1.48)
\end{aligned}}$$

The Poissonian stationary solution also follows from (7.1.13) by direct substitution.

e) Poissonian Time-Dependent Solutions

A very interesting property of this equation is the existence of *Poissonian time-dependent solutions*. For if we choose

$$P(x, 0) = \frac{e^{-\alpha_0}\alpha_0^x}{x!}, \tag{7.1.49}$$

then

$$G(s, 0) = \exp[(s-1)\alpha_0] \tag{7.1.50}$$

and from (7.1.32) we find

$$G(s, t) = \exp\{(s-1)[\alpha_0 e^{-k_1 t} + (k_2 a/k_1)(1 - e^{-k_1 t})]\} \tag{7.1.51}$$

corresponding to

$$P(x, t) = \frac{e^{-\alpha(t)}\alpha(t)^x}{x!} \tag{7.1.52}$$

with

$$\alpha(t) = \alpha_0 e^{-k_1 t} + (k_2 a/k_1)(1 - e^{-k_1 t}). \tag{7.1.53}$$

Here $\alpha(t)$ is seen to be the solution of the deterministic equation

$$\frac{dx}{dt} = k_2 a - k_1 x \tag{7.1.54}$$

with the initial condition $x(0) = \alpha_0$. (7.1.55)

This result can be generalised to many variables and forms the rationale for the *Poisson representation* which will be developed in Sect. 7.7. The existence of Poissonian propagating solutions is a consequence of the linearity of the system.

7.1.3 A Chemical Bistable System

We consider the system

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X \tag{7.1.56}$$

$$A \underset{k_4}{\overset{k_3}{\rightleftharpoons}} X \tag{7.1.57}$$

which has been studied by many authors [7.1]. The concentration of A is held fixed so that we have

$$\begin{aligned} t^+(x) &= k_1 A x(x-1) + k_3 A \\ t^-(x) &= k_2 x(x-1)(x-2) + k_4 x . \end{aligned} \tag{7.1.58}$$

The corresponding deterministic equation is, of course,

$$\begin{aligned} \frac{dx}{dt} &= t^+(x) - t^-(x) \\ &\simeq -k_2 x^3 + k_1 A x^2 - k_4 x + k_3 A , \end{aligned} \tag{7.1.59}$$

where it is assumed that $x \gg 1$ so that we set $x(x-1)(x-2) \simeq x^3$, etc. The solution of this equation, with the initial condition $x(0) = x_0$, is given by

$$\begin{aligned} &\left(\frac{x-x_1}{x_0-x_1}\right)^{x_3-x_2}\left(\frac{x-x_2}{x_0-x_2}\right)^{x_1-x_3}\left(\frac{x-x_3}{x_0-x_3}\right)^{x_2-x_1} \\ &\quad = \exp[-k_2(x_1-x_2)(x_2-x_3)(x_3-x_1)t] . \end{aligned} \tag{7.1.60}$$

Here, x_1, x_2, x_3 are roots of

$$k_2 x^3 - k_1 A x^2 + k_4 x - x_3 A = 0 \tag{7.1.61}$$

with $x_3 \geqslant x_2 \geqslant x_1$.

Clearly these roots are the stationary values of the solutions $x(t)$ of (7.1.59). From (7.1.59) we see that

$$\begin{aligned} x < x_1 \quad &\Longrightarrow \frac{dx}{dt} > 0 \\ x_2 > x > x_1 \quad &\Longrightarrow \frac{dx}{dt} < 0 \\ x_3 > x > x_2 \quad &\Longrightarrow \frac{dx}{dt} > 0 \\ x > x_3 \quad &\Longrightarrow \frac{dx}{dt} < 0 . \end{aligned} \tag{7.1.62}$$

Thus, in the region $x < x_2$, $x(t)$ will be attracted to x_1 and in the region $x > x_2$, $x(t)$ will be attracted to x_3. The solution $x(t) = x_2$ will be unstable to small perturbations. This yields a system with two deterministically stable stationary states.

a) Stochastic Stationary Solution

From (7.1.13)

$$P_s(x) = P_s(0) \prod_{z=1}^{x} \left\{\frac{B[(z-1)(z-2) + P]}{z(z-1)(z-2) + Rz}\right\}, \tag{7.1.63}$$

where

$$B = k_1A/k_2$$
$$R = k_4/k_2 \qquad (7.1.64)$$
$$P = k_3/k_1\,.$$

Notice that if $P = R$, the solution (7.1.63) is Poissonian with mean B. In this case, we have a stationary state in which reactions (7.1.56, 57) are simultaneously in balance. This is *chemical equilibrium*, in which, as we will show later, there is always a Poissonian solution (Sects. 7.5.1 and 7.7b). The maxima of (7.1.63) occur, according to (7.1.21), when

$$B = x[(x-1)(x-2) + R]/[P + x(x-1)]\,. \qquad (7.1.65)$$

The function $x = x(B)$, found by inverting (7.1.65), gives the maxima (or minima) corresponding to that value of B for a given P and R.

There are the two asymptotic forms:

$$\begin{aligned} &x(B) \sim B &&\text{large } B\\ &x(B) \sim PB/R &&\text{small } B \end{aligned} \qquad (7.1.66)$$

If $R > 9P$, we can show that the slope of $x(B)$ becomes negative for some range of $x > 0$ and thus we get three solutions for a given B, as shown in Fig. 7.1. The transition from one straight line to the other gives the kink that can be seen.

Notice also that for the choice of parameters shown, the bimodal shape is significant over a very small range of B. This range is very much narrower than the range over which $P(x)$ is two peaked, since the ratio of the heights of the peaks can be very high.

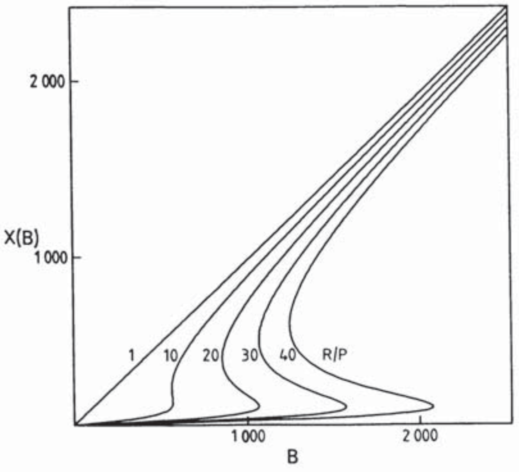

Fig. 7.1. Plot of $x(B)$ against B, as given by the solution of (7.1.65) for various values of R/P, and $P = 10{,}000$

A more precise result can be given. Suppose the volume V of the system becomes very large and the concentration y of X given by

$$y = x/V\,,$$

is constant. Clearly the transition probabilities must scale like V, since the rate of production of X will scale like $x = yV$.

Hence,

$$\begin{aligned} &k_1A \sim 1/V\\ &k_3A \sim V\\ &k_2 \sim 1/V^2\\ &k_4 \sim 1 \end{aligned} \qquad (7.1.67)$$

which means that

$$\begin{aligned} &B \sim V\\ &R \sim V^2\\ &P \sim V^2\,. \end{aligned} \qquad (7.1.68)$$

We then write

$$B = \tilde{B}V$$
$$R = \tilde{R}V^2$$
$$P = \tilde{P}V^2$$

so that (7.1.65) becomes

$$\tilde{B} \simeq y(y^2 + \tilde{R})/(y^2 + \tilde{P})\,.$$

And if y_1 and y_2 are two values of y,

$$\begin{aligned} \log[P_s(y_2)/P_s(y_1)] \simeq \sum_{z=y_1V}^{y_2V} \{&\log \tilde{B}V + \log(z^2 + \tilde{P}V^2)\\ &- \log[z(z^2 + \tilde{R}V^2)]\} \end{aligned} \qquad (7.1.69)$$

and we now approximate by an integral

$$\sim V\int_{y_1}^{y_2} dy \left[\log\left(\frac{\tilde{B}(y^2 + \tilde{P})}{y(y^2 + \tilde{R})}\right)\right].$$

Hence,

$$\frac{P_s(y_2)}{P_s(y_1)} \simeq \exp\left[V\int_{y_1}^{y_2} \log\left(\frac{\tilde{B}(y^2 + \tilde{P})}{y(y^2 + \tilde{R})}\right)\right] \qquad (7.1.70)$$

and as $V \to \infty$, depending on the sign of the integral, this ratio becomes either zero or infinity. Thus, in a large volume limit, the two peaks, unless precisely equal in height, become increasingly unequal and only one survives.

The variance of the distribution can be obtained by a simple trick. Notice from (7.1.63) that $P_s(x)$ can be written

$$P_s(x) = B^x G(x)\,, \tag{7.1.71}$$

where $G(x)$ is a function defined through (7.1.63). Then,

$$\left.\begin{aligned} &\langle x^k\rangle = \left[\sum_{x=0}^{\infty} x^k B^x G(x)\right]\left[\sum_{x=0}^{\infty} B^x G(x)\right]^{-1} \\ &\text{and} \\ &B\frac{\partial}{\partial B}\langle x^k\rangle = \langle x^{k+1}\rangle - \langle x\rangle\langle x^k\rangle \end{aligned}\right\} \tag{7.1.72}$$

so that

$$\operatorname{var}\{x\} = B\frac{\partial}{\partial B}\langle x\rangle\,. \tag{7.1.73}$$

From this we note that as $V \to \infty$,

$$\operatorname{var}\{y\} \sim \frac{1}{V} \to 0\,. \tag{7.1.74}$$

So a deterministic limit is approached. Further, notice that if $\langle x\rangle$ is proportional to B, the variance is equal to the mean, in fact, we find on the two branches (7.1.66),

$$\begin{aligned} \langle x(B)\rangle &= \operatorname{var}\{x(B)\} = B \qquad \text{large } B \\ \langle x(B)\rangle &= \operatorname{var}\{x(B)\} = PB/R \quad \text{small } B \end{aligned}$$

which means that the distributions are roughly Poissonian on these limiting branches.

The stochastic mean is not, in fact, given exactly by the peak values but approximates it very well. Of course, for any B there is one well defined $\langle x(B)\rangle$, not three values. Numerical computations show that the mean closely follows the lower branch and then suddenly makes a transition at B_c to the upper branch. This will be the value at which the two maxima have equal height and can, in principle, be determined from (7.1.70).

b) Time-Dependent Behaviour

This is impossible to deduce exactly. Almost all approximation methods depend on the large volume limit, whose properties in a stationary situation have just been noted and which will be dealt with systematically in the next section.

7.2 Approximation of Master Equations by Fokker-Planck Equations

The existence of the parameter V in terms of which well-defined scaling laws are valid leads to the concept of *system size expansions*, first put on a systematic basis by *van Kampen* [7.2]. There is a confused history attached to this, which arises out of repeated attempts to find a limiting form of the Master equation in which a Fokker-Planck equation arises. However, the fundamental result is that a diffusion proces can always be approximated by a jump process, not the reverse.

7.2.1 Jump Process Approximation of a Diffusion Process

The prototype result is that found for the random walk in Sect.3.8.2, that in the limit of infinitely small jump size, the Master equation becomes a Fokker-Planck equation. Clearly the jumps must become more probable and smaller, and this can be summarised by a *scaling assumption:* that there is a parameter δ, such that the average step size and the variance of the step size are proportional to δ, and such that the jump probabilities increase as δ becomes small.

We assume that the jump probabilities can be written

$$W_\delta(x'\,|\,x) = \Phi\left(\frac{x' - x - A(x)\delta}{\sqrt{\delta}},\, x\right)\delta^{-3/2}\,, \tag{7.2.1}$$

where

$$\int dy\,\Phi(y, x) = Q \tag{7.2.2}$$

and

$$\int dy\,y\,\Phi(y, x) = 0\,. \tag{7.2.3}$$

This means that

$$\begin{aligned} \alpha_0(x) &\equiv \int dx'\,W_\delta(x'\,|\,x) = Q/\delta \\ \alpha_1(x) &\equiv \int dx'(x' - x)W_\delta(x'\,|\,x) = A(x)Q \\ \alpha_2(x) &\equiv \int dx'(x' - x)^2 W_\delta(x'\,|\,x) = \int dy\,y^2\Phi(y, x)\,. \end{aligned} \tag{7.2.4}$$

We further assume that $\Phi(y, x)$ vanishes sufficiently rapidly as $y \to \infty$, so that

$$\lim_{\delta\to 0} W_\delta(x'\,|\,x) = \lim_{y\to\infty}\left[\left(\frac{y}{x' - x}\right)^3 \Phi(y, x)\right] = 0 \qquad \text{for} \quad x' \neq x\,. \tag{7.2.5}$$

The conditions (7.2.4, 5) are very similar to those in Sect.3.4, namely, (3.4.1, 4, 5) and by taking a twice differentiable function $f(z)$, one can carry out much the same procedure as that used in Sect. 3.4 to show that

$$\lim_{\delta\to 0}\left\langle\frac{\partial f(z)}{\partial t}\right\rangle = \left\langle \alpha_1(z)\frac{\partial f}{\partial z} + \frac{1}{2}\alpha_2(z)\frac{\partial^2 f}{\partial z^2}\right\rangle \tag{7.2.6}$$

implying that in the limit $\delta \to 0$, the Master equation

$$\frac{\partial P(x)}{\partial t} = \int dx'[W(x|x')P(x') - W(x'|x)P(x)] \tag{7.2.7}$$

becomes the FPE

$$\frac{\partial P(x)}{\partial t} = -\frac{\partial}{\partial x}\alpha_1(x)P(x) + \frac{1}{2}\frac{\partial^2}{\partial x^2}\alpha_2(x)P(x)\,. \tag{7.2.8}$$

Thus, given (7.2.8), one can always construct a Master equation depending on a parameter δ which approximates it as closely as desired. Such a Master equation will have transition probabilities which satisfy the criteria of (7.2.4). If they do *not* satisfy these criteria, then this approximation is not possible. Some examples are appropriate.

a) Random Walk (Sect.3.8.2)
Let $x = nl$, then

$$W(x|x') = d(\delta_{x',x-l} + \delta_{x',x+l})\,. \tag{7.2.9}$$

Then

$$\begin{aligned}\alpha_0(x) &= 2d\\ \alpha_1(x) &= 0\\ \alpha_2(x) &= 2l^2d\,;\end{aligned} \tag{7.2.10}$$

let

$$\delta = l^2 \tag{7.2.11}$$

and

$$D = l^2d\,. \tag{7.2.12}$$

Then all requirements are met, so the limiting equation is

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2} \tag{7.2.13}$$

as found in Sect.3.8.2.

b) Poisson Process (Sect.3.8.3)
Here, letting $x = nl$,

$$W(x|x') = d\delta_{x,x'+l} \tag{7.2.14}$$

and

$$\begin{aligned}\alpha_0(x) &= d\\ \alpha_1(x) &= ld\\ \alpha_2(x) &= l^2d\,.\end{aligned} \tag{7.2.15}$$

There is no way of parametrising l and d in terms of δ such that $l \to 0$ and both $\alpha_1(x)$ and $\alpha_2(x)$ are finite. In this case, there is no Fokker-Planck limit.

c) General Approximation of Diffusion Process by a Birth-Death Master Equation
Suppose we have a Master equation such that

$$W_\delta(x'|x) = \left(\frac{A(x)}{2\delta} + \frac{B(x)}{2\delta^2}\right)\delta_{x',x+\delta} + \left(-\frac{A(x)}{2\delta} + \frac{B(x)}{2\delta^2}\right)\delta_{x',x-\delta} \tag{7.2.16}$$

so that for sufficiently small δ, $W_\delta(x'|x)$ is positive and we assume that this is uniformly possible over the range of x of interest. The process then takes place on a range of x composed of integral multiples of δ. This is *not* of the form of (7.2.1) but, nevertheless, in the limit $\delta \to 0$ gives a FPE. For

$$\alpha_0(x) = B(x)/\delta^2 \tag{7.2.17a}$$

$$\alpha_1(x) = A(x) \tag{7.2.17b}$$

$$\alpha_2(x) = B(x) \tag{7.2.17c}$$

and

$$\lim_{\delta\to 0} W_\delta(x'|x) = 0 \qquad \text{for} \qquad x' \neq x\,. \tag{7.2.17d}$$

Here, however, $\alpha_0(x)$ diverges like $1/\delta^2$, rather than like $1/\delta$ as in (7.2.4) and the picture of a jump taking place according to a smooth distribution is no longer valid. The proof carries through, however, since the behaviour of $\alpha_0(x)$ is irrelevant and the limiting FPE is

$$\frac{\partial P(x)}{\partial t} = -\frac{\partial}{\partial x}A(x)P(x) + \frac{1}{2}\frac{\partial^2}{\partial x^2}B(x)P(x)\,. \tag{7.2.18}$$

In this form, we see that we have a possible tool for simulating a diffusion process by an approximating birth-death process. The method fails if $B(x) = 0$ anywhere in the range of x, since this leads to negative $W_\delta(x'|x)$. Notice that the stationary solution of the Master equation in this case is

$$\begin{aligned}P_s(x) &= P_s(0)\prod_{z=\delta}^{x}\left[\frac{\delta A(z-\delta) + B(z-\delta)}{-\delta A(z) + B(z)}\right]\\ &= P_s(0)\left[\frac{-\delta A(0) + B(0)}{\delta A(x) + B(x)}\right]\prod_{z=0}^{x}\left[\frac{1 + \delta A(z)/B(z)}{1 - \delta A(z)/B(z)}\right]\end{aligned} \tag{7.2.19}$$

so that, for small enough δ

$$\log P_s(x) \to \text{const} - \log B(x) + \sum_{z=0}^{x} 2\delta\, A(z)/B(z)\,, \tag{7.2.20}$$

i.e.,

$$P_s(x) \to \frac{\mathcal{N}}{B(x)} \exp\left[2\int_0^x dz\, A(z)/B(z)\right] \tag{7.2.21}$$

as required. The limit is clearly uniform in any finite interval of x provided $A(x)/B(x)$ is bounded there.

7.2.2 The Kramers-Moyal Expansion

A simple but nonrigorous derivation was given by *Kramers* [7.3] and considerably improved by *Moyal* [7.4]. It was implicitly used by *Einstein* [7.5] as explained in Sect. 1.2.1.

In the Master equation (7.2.7), we substitute x' by defining

$$\begin{aligned} &y = x - x' \quad \text{in the first term, and}\\ &y = x' - x \quad \text{in the second term.}\end{aligned}$$

Defining

$$t(y, x) = W(x + y\,|\,x)\,, \tag{7.2.22}$$

the master equation becomes

$$\frac{\partial P(x)}{\partial t} = \int dy\,[t(y, x - y)P(x - y) - t(y, x)P(x)]\,. \tag{7.2.23}$$

We now expand in power series,

$$= \int dy \sum_{n=1}^{\infty} \frac{(-y)^n}{n!} \frac{\partial^n}{\partial x^n}[t(y, x)P(x)] \tag{7.2.24}$$

$$= \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n}[\alpha_n(x)P(x)]\,, \tag{7.2.25}$$

where

$$\alpha_n(x) = \int dx'(x' - x)^n W(x'\,|\,x) = \int dy\, y^n\, t(y, x)\,. \tag{7.2.26}$$

By terminating the series (7.2.25) at the second term, we obtain the Fokker-Planck equation (7.2.8).

In introducing the system size expansion, van Kampen criticised this "proof", because there is no consideration of what small parameter is being considered.

Nevertheless, this procedure enjoyed wide popularity—mainly because of the convenience and simplicity of the result. However, the demonstration in Sect.7.2.1 shows that there are limits to its validity. Indeed, if we assume that $W(x'\,|\,x)$ has the form(7.2.1), we find that

$$\alpha_n(x) = \delta^{n/2-1} \int dy\, y^n \Phi(y, x)\,. \tag{7.2.27}$$

So that as $\delta \to 0$, terms higher than the second in the expansion (7.2.25) (*the Kramers-Moyal expansion*) do vanish. And indeed in his presentation, *Moyal* [7.4] did require conditions equivalent to (7.2.4, 5).

7.2.3 Van Kampen's System Size Expansion [7.2]

Birth-death master equations provide good examples of cases where the Kramers-Moyal expansion fails, the simplest being the Poisson process mentioned in Sect. 7.2.1.

In all of these, the size of the jump is ± 1 or some small integer, whereas typical sizes of the variable may be large, e.g., the number of molecules or the position of the random walker on a long lattice.

In such cases, we can introduce a system size parameter Ω such that the transition probabilities can be written in terms of the intensive variables x/Ω etc. For example, in the reaction of Sect.7.1.3, Ω was the volume V and x/Ω the concentration. Let us use van Kampen's notation:

a = extensive variable (number of molecules, etc $\propto \Omega$)

$x = a/\Omega$ intensive variable (concentration of molecules).

The limit of interest is large Ω at fixed x. This corresponds to the approach to a macroscopic system. We can rewrite the transition probability as

$$\begin{aligned} &W(a\,|\,a') = W(a'; \Delta a)\\ &\Delta a = a - a'.\end{aligned} \tag{7.2.28}$$

The essential point is that the size of the jump is expressed in terms of the extensive quantity Δa, but the dependence on a' is better expressed in terms of the intensive variable x.

Thus, we assume that we can write

$$W(a'; \Delta a) = \Omega\psi\left(\frac{a'}{\Omega}; \Delta a\right). \tag{7.2.29}$$

If this is the case, we can now make an expansion. We choose a new variable z so that

$$a = \Omega\phi(t) + \Omega^{1/2}z\,, \tag{7.2.30}$$

where $\phi(t)$ is a function to be determined. It will now be the case that the $\alpha_n(a)$ are proportional to Ω: we will write

$$\alpha_n(a) = \Omega\tilde{\alpha}_n(x)\,. \tag{7.2.31}$$

We now take the Kramers-Moyal expansion (7.2.25) and change the variable to get

$$\frac{\partial P(z,t)}{\partial t} - \Omega^{1/2}\phi'(t)\frac{\partial P(z,t)}{\partial z} = \sum_{n=1}^{\infty}\frac{\Omega^{1-n/2}}{n!} \times \left(-\frac{\partial}{\partial z}\right)^n \tilde{\alpha}_n[\phi(t) + \Omega^{-1/2}z]P(z,t). \tag{7.2.32}$$

The terms of order $\Omega^{1/2}$ on either side will cancel if $\phi(t)$ obeys

$$\phi'(t) = \tilde{\alpha}_1[\phi(t)] \tag{7.2.33}$$

which is the *deterministic equation* expected. We expand $\tilde{\alpha}_n[\phi(t) + \Omega^{-1/2}z]$ in powers of $\Omega^{-1/2}$, rearrange and find

$$\frac{\partial P(z,t)}{\partial t} = \sum_{m=2}^{\infty}\frac{\Omega^{-(m-2)/2}}{m!}\sum_{n=1}^{m}\frac{m!}{n!(m-n)!}\tilde{\alpha}_n^{(m-n)}[\phi(t)]\left(-\frac{\partial}{\partial z}\right)^n z^{m-n}P(z,t)\,. \tag{7.2.34}$$

Taking the large Ω limit, only the $m = 2$ term survives giving

$$\boxed{\frac{\partial P(z,t)}{\partial t} = -\,\tilde{\alpha}_1'[\phi(t)]\frac{\partial}{\partial z}z\,P(z,t) + \frac{1}{2}\tilde{\alpha}_2[\phi(t)]\frac{\partial^2}{\partial z^2}P(z,t)\,.} \tag{7.2.35}$$

a) Comparison with Kramers-Moyal Result

The Kramers-Moyal Fokker-Planck equation, obtained by terminating (7.2.25) after two terms, is

$$\frac{\partial P(a)}{\partial t} = -\frac{\partial}{\partial a}[\alpha_1(a)P(a)] + \frac{1}{2}\frac{\partial^2}{\partial a^2}[\alpha_2(a)P(a)] \tag{7.2.36}$$

and changing variables to $x = a/\Omega$, we get

$$\frac{\partial P(x)}{\partial t} = -\frac{\partial}{\partial x}[\tilde{\alpha}_1(x)P(x)] + \frac{1}{2\Omega}\frac{\partial^2}{\partial x^2}[\tilde{\alpha}_2(x)P(x)]\,. \tag{7.2.37}$$

We can now use the small noise theory of Sect. 6.3, with

$$\varepsilon^2 = \frac{1}{\Omega} \tag{7.2.38}$$

and we find that substituting

$$z = \Omega^{1/2}[x - \phi(t)]\,, \tag{7.2.39}$$

the lowest-order FPE for z is exactly the same as the lowest-order term in van Kampen's method (7.2.35). This means that if we are only interested in the lowest order, we may use the Kramers-Moyal Fokker-Planck equation which may be easier to handle than van Kampen's method. The results will differ, but to lowest order in $\Omega^{-1/2}$ will agree, and each will only be valid to this order.

Thus, if a FPE has been obtained from a Master equation, its validity depends on the kind of limiting process used to derive it. If it has been derived in a limit $\delta \to 0$ of the kind used in Sect.7.2.1, then it can be taken seriously and the full nonlinear dependence of $\alpha_1(a)$ and $\alpha_2(a)$ on a can be exploited.

On the other hand, if it arises as the result of an Ω expansion like that in Sect. 7.2.3, only the small noise approximation has any validity. There is no point in considering anything more than the linearisation, (7.2.35), about the deterministic solution. The solution of this equation is given in terms of the corresponding stochastic differential equation

$$dz = \tilde{\alpha}_1'[\phi(t)]z\,dt + \sqrt{\tilde{\alpha}_2[\phi(t)]}\,dW(t)\,. \tag{7.2.40}$$

by the results of Sect. 4.4.7 (4.4.69), or Sect. 4.4.9 (4.4.83).

b) Example: Chemical Reaction $X \rightleftharpoons A$

From Sect. 7.1.2, we have

$$W(x\,|\,x') = \delta_{x,x'+1}k_2a + \delta_{x,x'-1}k_1x'\,. \tag{7.2.41}$$

The assumption is

$$\begin{aligned} a &= a_0V \\ x &= x_0V\,, \end{aligned} \tag{7.2.42}$$

where V is the volume of the system. This means that we assume the total amounts of A and X to be proportional to V (a reasonable assumption) and that the rates of production and decay of X are proportional to a and x, respectively.

Thus,

$$W(x_0';\,\Delta x) = V[k_2a_0\delta_{\Delta x,1} + k_1x_0'\delta_{\Delta x,-1}] \tag{7.2.43}$$

which is in the form of (7.2.29), with $\Omega \to V$, $a \to x$, etc.
Thus,

$$\begin{aligned} \alpha_1(x) &= \sum(x' - x)W(x'\,|\,x) = k_2a - k_1x = V(k_2a_0 - k_1x_0) \\ \alpha_2(x) &= \sum(x' - x)^2W(x'\,|\,x) = k_2a + k_1x = V(k_2a_0 + k_1x_0)\,. \end{aligned} \tag{7.2.44}$$

The deterministic equation is

$$\phi'(t) = [k_2a_0 - k_1\phi(t)] \tag{7.2.45}$$

whose solutions is

$$\phi(t) = \phi(0)e^{-k_1t} + \frac{k_2a_0}{k_1}(1 - e^{-k_1t})\,. \tag{7.2.46}$$

The Fokker-Planck equation is

$$\frac{\partial P(z)}{\partial t} = k_1 \frac{\partial}{\partial z} zP(z) + \frac{1}{2}\frac{\partial^2}{\partial z^2}[k_2 a_0 + k_1\phi(t)]P(z)\,. \tag{7.2.47}$$

From (4.4.84, 85) we can compute that

$$\langle z(t)\rangle = z(0)\mathrm{e}^{-k_1 t}\,. \tag{7.2.48}$$

Usually, one would assume $z(0) = 0$, since the initial condition can be fully dealt with by the initial condition on ϕ. Assuming $z(0)$ is zero, we find

$$\operatorname{var}\{z(t)\} = \left[\frac{k_2 a_0}{k_1} + \phi(0)\mathrm{e}^{-k_1 t}\right](1 - \mathrm{e}^{-k_1 t}) \tag{7.2.49}$$

so that

$$\langle x(t)\rangle = V\phi(t) = V\phi(0)\mathrm{e}^{-k_1 t} + \frac{k_2 a}{k_1}(1 - \mathrm{e}^{-k_1 t}) \tag{7.2.50}$$

$$\operatorname{var}\{x(t)\} = V \operatorname{var}\{z(t)\} = \left[\frac{k_2 a}{k_1} + V\phi(0)\mathrm{e}^{-k_1 t}\right](1 - \mathrm{e}^{-k_1 t})\,. \tag{7.2.51}$$

With the identification $V\phi(0) = N$, these are exactly the same as the exact solutions (7.1.38–40) in Sect. 7.1.2. The stationary solution of (7.2.47) is

$$P_s(z) = \mathscr{N} \exp\left(-\frac{k_1 z^2}{2k_2 a_0}\right) \tag{7.2.52}$$

which is Gaussian approximation to the exact Poissonian.

The stationary solution of the Kramers-Moyal equation is

$$\begin{aligned} P_s(x) &= \frac{\mathscr{N}}{\alpha_2(x)} \exp\left[\int_0^x 2\frac{\alpha_1(x')}{\alpha_2(x')}dx'\right] \\ &= \mathscr{N}(k_2 a + k_1 x)^{-1+4k_2 a/k_1}\mathrm{e}^{-2x}\,. \end{aligned} \tag{7.2.53}$$

In fact, one can explicitly check the limit by setting

$$x = V(k_2 a_0/k_1) + \delta \tag{7.2.54}$$

so that

$$(7.2.53) \simeq \mathscr{N}(2Vk_2 a_0 + k_1\delta)^{-1+4Vk_2 a_0/k_1}\mathrm{e}^{-2Vk_2 a_0/k_1 - 2\delta}\,. \tag{7.2.55}$$

Then,

$$\log P_s(x) \simeq \text{const} - \frac{k_2}{2k_2 a_0 V}(\delta - \delta^2)\,. \tag{7.2.56}$$

Using the exact Poissonian solution, making the same substitution and using Stirling's formula

$$\log x! \sim (x + \tfrac{1}{2})\log x - x + \text{const}\,, \tag{7.2.57}$$

one finds the same result as (7.2.56), but the exact results are different, in the sense that even the ratio of the logarithms is different.

The term linear in δ is, in fact, of lower order in V: because using (7.2.39), we find $\delta = z\sqrt{V}$ and

$$\log P_s(z) \sim \text{const} - \frac{k_1}{2k_2 a_0}\left(\frac{z}{\sqrt{V}} - z^2\right) \tag{7.2.58}$$

so that in the large V limit, we have a simple Gaussian with zero mean.

c) Moment Hierarchy

From the expansion (7.2.34), we can develop equations for the moments

$$\langle z^k\rangle = \int dz\, P(z,t)z^k \tag{7.2.59}$$

by direct substitution and integration by parts:

$$\frac{d}{dt}\langle z^k\rangle = \sum_{m=2}^{\infty}\frac{\Omega^{-(m-2)/2}}{m!}\sum_{n=1}^{m,k}\frac{m!k!}{n!(m-n)!(k-n)!}\tilde{\alpha}_n^{(m-n)}[\phi(t)]\langle z^{m+k-2n}\rangle\,. \tag{7.2.60}$$

One can develop a hierarchy by expanding $\langle z^k\rangle$ in inverse powers of $\Omega^{1/2}$:

$$\langle z^k\rangle = \sum_{r=0}^{\infty} M_r^k \Omega^{-r/2}\,. \tag{7.2.61}$$

From such a hierarchy one can compute stationary moments and autocorrelation functions using the same techniques as those used in handling the moment hierarchy for the small noise expansion of the Fokker-Planck equation in Sect.6.3.1. *Van Kampen* [7.2] has carried this out.

7.2.4 Kurtz's Theorem

Kurtz [7.6] has demonstrated that in a certain sense, the Kramers-Moyal expansion can give rise to a slightly stronger result than van Kampen's expansion. For the restricted class of birth-death processes with polynomial transition probabilities, he has shown the following. We consider the stochastic process obeying a birth-death master equation

$$\partial_t P(a,t) = \sum_{a'} W(a|a')P(a',t) - \sum_{a'} W(a'|a)P(a,t) \tag{7.2.62}$$

in which the scaling condition (7.2.29) is satisfied.

Then the process $b(t)$, satisfying the stochastic differential equation

$$db(t) = \alpha_1(b)dt + \sqrt{\alpha_2(b)}\, dW(t) \tag{7.2.63}$$

exists, and to each sample path $a(t)$ of (7.2.62) a sample path of $b(t)$ of (7.2.63) exists such that

$$|b(t) - a(t)| \sim \log V \tag{7.2.64}$$

for all *finite t*.

This result implies the lowest order result of van Kampen. For, we make the the substitution of the form (7.2.30)

$$a(t) = V\phi(t) + V^{1/2}z(t) \tag{7.2.65}$$

$$b(t) = V\phi(t) + V^{1/2}y(t)\,. \tag{7.2.66}$$

Then the characteristic function of $z(t)$ is

$$\begin{aligned}\langle \exp[isz(t)]\rangle &= \langle \exp[isV^{-1/2}a(t) - isV^{1/2}\phi(t)]\rangle \\ &= \exp[-isV^{1/2}\phi(t)]\langle \exp[isV^{-1/2}b(t)]\rangle + O(V^{-1/2}\log V) \\ &= \langle \exp[isy(t)]\rangle + O(V^{-1/2}\log V)\,.\end{aligned} \tag{7.2.67}$$

Using now the asymptotic expansion for the FPE we know the distribution function of $y(t)$ approaches that of the FPE (7.2.35) to $O(V^{-1/2})$ and the result follows with, however, a slightly weaker convergence because of the log V term involved. Thus, in terms of quantities which can be calculated and measured, means, variances, etc, Kurtz's apparently stronger result is equivalent to van Kampen's system size expansion.

7.2.5 Critical Fluctuations

The existence of a system size expansion as outlined in Sect.7.2.3 depends on the fact that $\tilde{\alpha}_1'(a)$ does not vanish. It is possible, however, for situations to arise where

$$\tilde{\alpha}_1'(\phi_s) = 0\,, \tag{7.2.68}$$

where ϕ_s is a stationary solution of the deterministic equation. This occurs, for example, when we consider the reaction of Sect.7.1.3 for which (using the notation of that section)

$$\tilde{\alpha}_1(y) = (\tilde{B}y^2 + \tilde{p} - y^3 - y\tilde{R})\tilde{k}_2\,,$$

where $\tilde{k}_2 = V^2k_2$.

Two situations can occur, corresponding to A and B in Fig. 7.2. The situation A corresponds to an unstable stationary state—any perturbation to the left will eventually lead to C, but B is stable. Clearly the deterministic equation takes the form

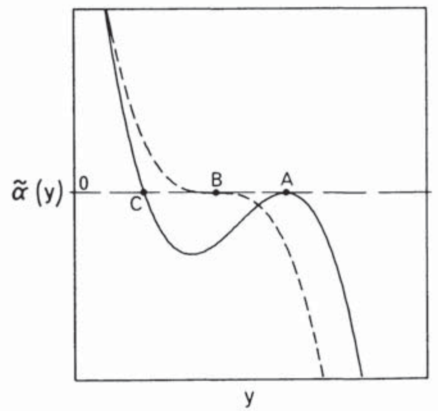

Fig. 7.2. Graph showing different kinds of behaviour of $\alpha_1(y)$ which lead to $\alpha_1'(y) = 0$

$$\dot{y} = -\tilde{k}_2(y - \phi_s)^3 \tag{7.2.69}$$

and we have a Master equation analogue of the cubic process of Sect.6.2.4a.

Van Kampen [7.13] has shown that in this case we should write

$$a = \Omega\,\phi(t) + \Omega^\mu u \tag{7.2.70}$$

in which case (7.2.32) becomes

$$\frac{\partial P(z,t)}{\partial t} - \Omega^{1-\mu}\phi'(t)\frac{\partial P(z,t)}{\partial z} = \sum_{n=1}^{\infty}\frac{\Omega^{1-\mu n}}{n!}\left(-\frac{\partial}{\partial z}\right)^n\tilde{\alpha}_n[\phi(t) + \Omega^{\mu-1}z]P(z,t)\,. \tag{7.2.71}$$

Suppose now that the first $q - 1$ derivatives of $\tilde{\alpha}_1(\phi_s)$ vanish. Then if we choose ϕ_s for $\phi(t)$, (7.2.71) becomes to lowest order

$$\begin{aligned}\frac{\partial P(z,t)}{\partial t} = &-\frac{1}{q!}\tilde{\alpha}_1^{(q)}(\phi_s)\Omega^{(1-q)(1-\mu)}\frac{\partial}{\partial z}(z^q p) \\ &+ \tfrac{1}{2}\alpha_2(\phi_s)\Omega^{1-2\mu}\frac{\partial^2 p}{\partial z^2} + \text{higher terms.}\end{aligned} \tag{7.2.72}$$

To make sure z remains of order unity, set

$$(1-q)(1-\mu) = (1-2\mu), \text{ i.e., } \mu = \frac{q}{q+1} \tag{7.2.73}$$

so the result is

$$\frac{\partial P}{\partial t} = \Omega^{-(q-1)/(q+1)}\left(-\frac{1}{q!}\tilde{\alpha}_1^{(q)}\frac{\partial}{\partial z}z^q p + \tfrac{1}{2}\tilde{\alpha}_2\frac{\partial^2 P}{\partial z^2}\right) \tag{7.2.74}$$

(where $\tilde{\alpha}_1^{(q)}$ and $\tilde{\alpha}_2$ are evaluated at ϕ_s.) The fluctuations now vary on a slower time scale τ given by

$$\tau = t\Omega^{-(q-1)/(q+1)} \tag{7.2.75}$$

and the equation for the average is

$$\frac{d\langle x\rangle}{d\tau} = \frac{1}{q!}\tilde{\alpha}_1^{(q)}\langle x^q\rangle \tag{7.2.76}$$

which is no longer that associated with the linearised deterministic equation. Of course, stability depends on the sign of $\tilde{\alpha}_1^{(q)}$ and whether q is odd or even. The simplest stable case occurs for $q = 3$ which occurs at the critical point B of Fig.7.2, and in this case we have the cubic process of Sect.6.3.4a. The long-time scale is

$$\tau = \Omega^{-1/2}t\,. \tag{7.2.77}$$

We see that for large Ω, the system's time dependence is given as a function of $\tau = \Omega^{-1/2}t$. Only for times $t \gtrsim \Omega^{1/2}$ does τ become a significant size, and thus it is only for very long times t that any significant time development of the system takes place. Thus, the motion of the system becomes *very slow* at large Ω.

The condition (7.2.68) is normally controllable by some external parameter, (say, for example, the temperature), and the point in the parameter space where (7.2.68) is satisfied is called a *critical point*. This property of very slow time development at a critical point is known as *critical slowing down.*

7.3 Boundary Conditions for Birth-Death Processes

For birth-death processes, we have a rather simple way of implementing boundary conditions. For a process confined within an interval $[a, b]$, it is clear that reflecting and absorbing boundary conditions are obtained by forbidding the exit from the interval or the return to it, respectively. Namely,

	Reflecting	Absorbing
Boundary at a	$t^-(a) = 0$	$t^+(a-1) = 0$
Boundary at b	$t^+(b) = 0$	$t^-(b+1) = 0.$

(7.3.1)

It is sometimes useful, however, to insert boundaries in a process and, rather than set certain transition probabilities equal to zero, impose boundary conditions similar to those used for Fokker-Planck equations (Sect.5.2.1) so that the resulting solution in the interval $[a, b]$ is a solution of the Master equation with the appropriate vanishing transition probabilities. This may be desired in order to preserve the particular analytic form of the transition probabilities, which may have a certain convenience.

a) Forward Master Equation

We can write the forward Master equation as

$$\begin{aligned}\partial_t P(x, t|x', t') = {}& t^+(x-1)P(x-1, t|x', t') + t^-(x+1)P(x+1, t|x', t') \\ & - [t^+(x) + t^-(x)]P(x, t|x', t')\,.\end{aligned} \tag{7.3.2}$$

Suppose we want a reflecting barrier at $x = a$. Then this could be obtained by requiring

$$t^-(a) = 0$$

and

$$P(a-1, t|x', t) = 0\,. \tag{7.3.3}$$

The only equation affected by this requirement is that for $\partial_t P(a, t|x', t')$ for which the same equation can be obtained by not setting $t^-(a) = 0$ but instead introducing a *fictitious* $P(a-1, t|x', t')$ such that

$$t^+(a-1)P(a-1, t|x', t') = t^-(a)P(a, t|x', t')\,. \tag{7.3.4}$$

This can be viewed as the analogue of the zero current requirement for a reflecting barrier in a Fokker-Planck equation.

If we want an absorbing barrier at $x = a$, we can set

$$t^+(a-1) = 0\,. \tag{7.3.5}$$

After reaching the point $a - 1$, the process never returns and its behaviour is now of no interest. The only equation affected by this is that for $\partial_t P(a, t|x', t')$ and the same equation can be again obtained by introducing a *fictitious* $P(a-1, t|x', t')$ such that

$$P(a-1, t|x', t') = 0\,. \tag{7.3.6}$$

Summarising, we have the alternative formulation of imposed boundary conditions which yield the same effect in $[a, b]$ as (7.3.1):

Foward Master Equation on interval $[a, b]$	Reflecting	Absorbing
Boundary at a	$t^-(a)P(a) = t^+(a-1)P(a-1)$	$P(a-1) = 0$
Boundary at b	$t^+(b)P(b) = t^-(b+1)P(b+1)$	$P(b+1) = 0$

(7.3.7)

b) Backward Master Equation

The backward Master equation is (see Sect. 3.6)

$$\begin{aligned}\partial_{t'} P(x, t|x', t') = {}& t^+(x')[P(x, t|x'+1, t') - P(x, t|x', t')] \\ & + t^-(x')[P(x, t|x'-1, t') - P(x, t|x', t')]\,.\end{aligned} \tag{7.3.8}$$

In the case of a reflecting barrier, at $x = a$, it is clear that $t^-(a) = 0$ is equivalent to constructing a fictitious $P(x, t|a-1, t')$ such that

$$P(x, t|a-1, t') = P(x, t|a, t') \tag{7.3.9}$$

In the absorbing barrier case, none of the equations for $P(x,t\,|\,x',t')$ with $x,x' \in [a,b]$ involve $t^+(a-1)$. However, because $t^+(a-1)=0$, the equations in which $x' < a-1$ will clearly preserve the condition

$$P(x,t\,|\,x',t') = 0, \qquad x \in [a,b], \qquad x' \leqslant a-1 \tag{7.3.10}$$

and the effect of this on the equation with $x' = a$ will be to impose

$$P(x,t\,|\,a-1,t') = 0 \tag{7.3.11}$$

which is therefore the required boundary condition. Summarising:

Backward Master Equation on interval $[a, b]$	Reflecting	Absorbing
Boundary at a	$P(\cdot\,\|\,a-1) = P(\cdot\,\|\,a)$	$P(\cdot\,\|\,a-1) = 0$
Boundary at b	$P(\cdot\,\|\,b+1) = P(\cdot\,\|\,b)$	$P(\cdot\,\|\,b+1) = 0$

(7.3.12)

7.4 Mean First Passage Times

The method for calculating these in the simple one-step case parallels that of the Fokker-Planck equation (Sect.5.2.7) very closely. We assume the system is confined to the range

$$a \leqslant x \leqslant b \tag{7.4.1}$$

and is abosrbed or reflected at either end, as the case may be. For definiteness we take a system with

reflecting barrier at $x = a$;
absorbing state at $x = b + 1$.

The argument is essentially the same as that in Sect.5.2.7 and we find that $T(x)$, the mean time for a particle initially at x to be absorbed, satisfies the equation related to the *backward Master equation* (7.3.8):

$$t^+(x)[T(x+1) - T(x)] + t^-(x)[T(x-1) - T(x)] = -1 \tag{7.4.2}$$

with the boundary condition corresponding to (5.2.159) and arising from (7.3.12):

$$T(a-1) = T(a) \tag{7.4.3a}$$

$$T(b+1) = 0\,. \tag{7.4.3b}$$

Define

$$U(x) = T(x+1) - T(x) \tag{7.4.4}$$

so (7.4.2) becomes

$$t^+(x)U(x) - t^-(x)U(x-1) = 1\,. \tag{7.4.5}$$

Define

$$\phi(x) = \prod_{z=a+1}^{x} \frac{t^-(z)}{t^+(z)} \qquad \text{and} \tag{7.4.6}$$

$$S(x) = U(x)/\phi(x) \tag{7.4.7}$$

then (7.4.5) is equivalent to

$$t^+(x)\phi(x)[S(x) - S(x-1)] = -1 \tag{7.4.8}$$

with a solution

$$S(x) = -\sum_{z=a}^{x} 1/[t^+(z)\phi(z)]\,. \tag{7.4.9}$$

This satisfies the boundary condition (7.4.3a) which implies that

$$U(a-1) = S(a-1) = 0\,. \tag{7.4.10}$$

Hence,

$$T(x+1) - T(x) = -\phi(x)\sum_{z=a}^{x} 1/[t^+(z)\phi(z)] \tag{7.4.11}$$

and

$$\boxed{T(x) = \sum_{y=x}^{b} \phi(y) \sum_{z=a}^{y} 1/[t^+(z)\phi(z)]} \quad \begin{array}{l} a \ \text{ reflecting} \\ b \ \text{ absorbing} \\ b > a \end{array} \tag{7.4.12}$$

which also satisfies the boundary condition $T(b+1) = 0$, (7.4.3b).
Similarly, if a is absorbing and b reflecting

$$\boxed{T(x) = \sum_{y=a}^{x} \phi(y) \sum_{z=y}^{b} 1/[t^+(z)\phi(z)]} \quad \begin{array}{l} a \ \text{ absorbing} \\ b \ \text{ reflecting} \\ b > a \end{array} \tag{7.4.13}$$

and a formula corresponding to (5.2.158) for both a and b absorbing can be similarly deduced.

7.4.1 Probability of Absorption

The mean time to absorption is always finite when a and b are finite. If, however, b is at infinity and is reflecting, the mean time may diverge. This does not itself mean that there is a finite probability of not being absorbed. The precise result [Ref. 7.7, Sect.4.7] is the following.

If the process takes place on the interval (a, ∞) and a is absorbing, then the probability of absorption into state $a - 1$ from state x is given as follows. Define the function $M(x)$ by

$$M(x) = \sum_{y=a}^{\infty}\left[\prod_{z=a}^{y} \frac{t^+(y)}{t^-(y)}\right]. \tag{7.4.14}$$

Then if $M(x) < \infty$, the probability of absorption at $a - 1$, from state x, is

$$\frac{M(x)}{1 + M(x)} \tag{7.4.15}$$

and if $M(x) = \infty$, this probability is one. If this probability is 1, then the mean time to absorption is (7.4.13).

7.4.2 Comparison with Fokker-Planck Equation

The formulae (7.4.12, 13) are really very similar to the corresponding formulae (7.4.1, 2) for a diffusion process. In fact, using the model of Sect. 7.2.1c it is not difficult to show that in the limit $\delta \to 0$ the two become the same.

If we wish to deal with the kind of problem related to escape over a potential barrier (Sect.5.2.7c) which turn up in the context of this kind of master equation, for example, in the bistable reaction discussed in Sect.7.1.3, very similar approximations can be made. In this example, let us consider the mean first passage time from the stable stationary state x_1 to the other stable stationary state x_3.

Then the point $x = 0$ is a reflecting barrier, so the interval under consideration is $(0, x_3)$ with initial point x_1. Notice that

$$\phi(x) = \prod_{z=1}^{x} \frac{t^-(z)}{t^+(z)} = \frac{P_s(0)\,t^+(0)}{P_s(x)\,t^+(x)} \tag{7.4.16}$$

so that

$$T(x_1 \to x_3) = \sum_{y=x_1}^{x_3} [P_s(y)t^+(y)]^{-1} \sum_{z=0}^{y} P_s(z)\,. \tag{7.4.17}$$

If we assume that $P_s(y)^{-1}$ has a *sharp* maximum at the unstable point x_2, we can set $y = x_2$ in all other factors in (7.4.17) to obtain

$$T(x_1 \to x_3) \sim \frac{n_1}{t^+(x_2)} \sum_{y=x_1}^{x_3} [P_s(y)]^{-1}\,, \tag{7.4.18}$$

$$n_1 = \sum_{z=0}^{x_2} P_s(z) \tag{7.4.19}$$

and is the total probability of being in the lower peak of the stationary distribution. The result is a discrete analogue of those obtained in Sect. 5.2.7c.

7.5 Birth-Death Systems with Many Variables

There is a very wide class of systems whose time development can be considered as the result of individual encounters between members of some population. These include, for example,

—chemical reactions, which arise by transformations of molecules on collision;
—population systems, which die, give birth, mate and consume each other;
—systems of epidemics, in which diseases are transmitted from individual to individual by contact.

All of these can usually be modelled by what I call *combinatorial kinetics*, in which the transition probability for a certain transformation consequent on that encounter is proportional to the number of possible encounters of that type.

For example, in a chemical reaction $X \rightleftharpoons 2Y$, the reaction $X \to 2Y$ occurs by spontaneous decay, a degenerate kind of encounter, involving only one individual. The number of encounters of this kind is the number of X; hence, we say

$$t(x \to x - 1, y \to y + 2) = k_1 x\,. \tag{7.5.1}$$

For the reverse reaction, one can assemble pairs of molecules of Y in $y(y - 1)/2$ different ways. Hence

$$t(x \to x + 1, y \to y - 2) = k_2 y(y - 1)\,. \tag{7.5.2}$$

In general, we can consider encounters of many kinds between molecules, species, etc., of many kinds. Using the language of chemical reactions, we have the general formulation as follows.

Consider an n-component reacting system involving s different reactions:

$$\sum_a N_a^A X_a \underset{k_A^-}{\overset{k_A^+}{\rightleftharpoons}} \sum_a M_a^A X_a \qquad (A = 1, 2, \dots, s)\,. \tag{7.5.3}$$

The coefficient N_a^A of X_a is the number of molecules of X_a involved on the left and M_a^A is the number involved on the right. We introduce a vector notation so that if x_a is the number of molecules of X_a, then

$$\begin{aligned} \boldsymbol{x} &= (x_1, x_2, \dots, x_n) \\ \boldsymbol{N}^A &= (N_1^A, N_2^A, \dots, N_n^A) \\ \boldsymbol{M}^A &= (M_1^A, M_2^A, \dots, M_n^A) \end{aligned} \tag{7.5.4}$$

and we also define

$$\boldsymbol{r}^A = \boldsymbol{M}^A - \boldsymbol{N}^A\,. \tag{7.5.5}$$

Clearly, as reaction A proceeds one step in the forward direction,

$$\boldsymbol{x} \to \boldsymbol{x} + \boldsymbol{r}^A \tag{7.5.6}$$

and in the backward direction,

$$\boldsymbol{x} \to \boldsymbol{x} - \boldsymbol{r}^A\,. \tag{7.5.7}$$

The rate constants are defined by

$$\begin{aligned} t_A^+(\boldsymbol{x}) &= k_A^+ \prod_a \frac{x_a!}{(x_a - N_a^A)!} \\ t_A^-(\boldsymbol{x}) &= k_A^- \prod_a \frac{x_a!}{(x_a - M_a^A)!} \end{aligned} \tag{7.5.8}$$

which are proportional, respectively, to the number of ways of choosing the combination $\boldsymbol{N}^A$ or $\boldsymbol{M}^A$ from $\boldsymbol{x}$ molecules. The Master equation is thus

$$\begin{aligned} \partial_t P(\boldsymbol{x}, t) = \sum_A \{ & [t_A^-(\boldsymbol{x} + \boldsymbol{r}^A) P(\boldsymbol{x} + \boldsymbol{r}^A, t) - t_A^+(\boldsymbol{x}) P(\boldsymbol{x}, t)] \\ & + [t_A^+(\boldsymbol{x} - \boldsymbol{r}^A) P(\boldsymbol{x} - \boldsymbol{r}^A, t) - t_A^-(\boldsymbol{x}) P(\boldsymbol{x}, t)]\}\,. \end{aligned} \tag{7.5.9}$$

This form is, of course, a completely general way of writing a time-homogeneous Master equation for an integer variable $\boldsymbol{x}$ in which steps of size $\boldsymbol{r}^A$ can occur. It is only by making the special choice (7.5.8) for the transition probabilities per unit time that the general *combinatorial Master equation* arises. Another name is the *chemical Master equation*, since such equations are particularly adapted to chemical reactions.

7.5.1 Stationary Solutions when Detailed Balance Holds

In general, there is no explicit way of writing the stationary solution in a practical form. However, if detailed balance is satisfied, the stationary solution is easily derived. The variable $\boldsymbol{x}$, being simply a vector of numbers, can only be an even variable, hence, detailed balance must take the form (from Sect. 5.3.5)

$$t_A^-(\boldsymbol{x} + \boldsymbol{r}^A) P_s(\boldsymbol{x} + \boldsymbol{r}^A) = t_A^+(\boldsymbol{x}) P_s(\boldsymbol{x}) \tag{7.5.10}$$

for all A. The requirement that this holds for all A puts quite stringent requirements on the $t_A^\pm$. This arises from the fact that (7.5.10) provides a way of calculating $P_s(\boldsymbol{x}_0 + n\boldsymbol{r}^A)$ for any n and any initial $\boldsymbol{x}_0$. Using this method for all available A, we can generate $P_s(\boldsymbol{x})$ on the space of all $\boldsymbol{x}$ which can be written

$$\boldsymbol{x} = \boldsymbol{x}_0 + \sum n_A \boldsymbol{r}^A\,; \qquad (n_A \text{ integral}) \tag{7.5.11}$$

but the solutions obtained may be ambiguous since, for example, from (7.5.10) we may write

$$\left.\begin{aligned} & P_s[(\boldsymbol{x} + \boldsymbol{r}^A) + \boldsymbol{r}^B] = \frac{P_s(\boldsymbol{x})\, t_A^+(\boldsymbol{x})\, t_B^+(\boldsymbol{x} + \boldsymbol{r}^A)}{t_A^-(\boldsymbol{x} + \boldsymbol{r}^A)\, t_B^-(\boldsymbol{x} + \boldsymbol{r}^A + \boldsymbol{r}^B)} \\ & \text{but} \\ & P_s[(\boldsymbol{x} + \boldsymbol{r}^B) + \boldsymbol{r}^A] = \frac{P_s(\boldsymbol{x})\, t_B^+(\boldsymbol{x})\, t_A^+(\boldsymbol{x} + \boldsymbol{r}^B)}{t_B^-(\boldsymbol{x} + \boldsymbol{r}^B)\, t_A^-(\boldsymbol{x} + \boldsymbol{r}^A + \boldsymbol{r}^B)} \end{aligned}\right\} \tag{7.5.12}$$

Using the combinatorial forms (7.5.8) and substituting in (7.5.12), we find that this condition is automatically satisfied.

The condition becomes nontrivial when the same two points can be connected to each other in two essentially different ways, i.e., if, for example,

$$\begin{aligned} & \boldsymbol{N}^A \neq \boldsymbol{N}^B \\ & \boldsymbol{M}^A \neq \boldsymbol{M}^B \end{aligned} \tag{7.5.13}$$

but $\boldsymbol{r}^A = \boldsymbol{r}^B \equiv \boldsymbol{r}\,.$

In this case, uniqueness of $P_s(\boldsymbol{x} + \boldsymbol{r}^A)$ in (7.5.10) requires

$$\frac{t_A^+(\boldsymbol{x})}{t_A^-(\boldsymbol{x} + \boldsymbol{r})} = \frac{t_B^+(\boldsymbol{x})}{t_B^-(\boldsymbol{x} + \boldsymbol{r})} \tag{7.5.14}$$

and this means

$$\frac{k_A^+}{k_A^-} = \frac{k_B^+}{k_B^-}\,. \tag{7.5.15}$$

If there are two chains $A, B, C, \ldots$, and $A', B', C', \ldots$, of reactions such that

$$\boldsymbol{r}^A + \boldsymbol{r}^B + \boldsymbol{r}^C + \ldots = \boldsymbol{r}^{A'} + \boldsymbol{r}^{B'} + \boldsymbol{r}^{C'} + \ldots\,. \tag{7.5.16}$$

Direct substitution shows that

$$P_s(\boldsymbol{x} + \boldsymbol{r}^A + \boldsymbol{r}^B + \boldsymbol{r}^C + \ldots) = P_s(\boldsymbol{x} + \boldsymbol{r}^{A'} + \boldsymbol{r}^{B'} + \boldsymbol{r}^{C'} + \ldots) \tag{7.5.17}$$

only if

$$\boxed{\frac{k_A^+}{k_A^-}\frac{k_B^+}{k_B^-}\frac{k_C^+}{k_C^-}\cdots = \frac{k_{A'}^+}{k_{A'}^-}\frac{k_{B'}^+}{k_{B'}^-}\frac{k_{C'}^+}{k_{C'}^-}\cdots} \tag{7.5.18}$$

which is, therefore, the condition for detailed balance in a Master equation with combinatorial kinetics.

A solution for $P_s(\boldsymbol{x})$ in this case is a multivariate Poisson

$$P_s(\boldsymbol{x}) = \prod_a \frac{\alpha_a^{x_a} e^{-\alpha_a}}{x_a!} \tag{7.5.19}$$

which we check by substituting into (7.5.10) which gives

$$\prod_a \frac{\alpha_a{}^{(x_a+r_a^A)}\mathrm{e}^{-\alpha_a}}{(x_a+r_a^A)!}\frac{k_A^-(x_a+r_a^A)!}{(x_a+r_a^A-M_a^A)!}=\prod_a\frac{\alpha_a^{x_a}\,\mathrm{e}^{-\alpha_a}}{x_a!}\frac{k_A^+\,x_a!}{(x_a-N_a^A)!}\,. \tag{7.5.20}$$

Using the fact that

$$r_a^A = M_a^A - N_a^A\,,$$

we find that

$$k_A^+ \prod_a \alpha_a{}^{N_a^A} = k_A^- \prod_a \alpha_a{}^{M_a^A}\,. \tag{7.5.21}$$

However, the most general solution will have this form only subject to conservation laws of various kinds. For example, in the reaction

$$X \rightleftharpoons 2Y\,, \tag{7.5.22}$$

the quantity $2x + y$ is conserved. Thus, the stationary distribution is

$$\frac{\mathrm{e}^{-\alpha_1}\,\alpha_1^x}{x!}\frac{\mathrm{e}^{-\alpha_2}\,\alpha_2^y}{y!}\phi(2x+y) \tag{7.5.23}$$

where ϕ is an arbitrary function. Choosing $\phi(2x + y) = 1$ gives the Poissonian solution. Another choice is

$$\phi(2x+y) = \delta(2x+y, N) \tag{7.5.24}$$

which corresponds to fixing the total of $2x + y$ at N.

As a degenerate form of this, one sometimes considers a reaction written as

$$A \rightleftharpoons 2Y \tag{7.5.25}$$

in which, however, A is considered a fixed, deterministic number and the possible reactions are

$$\begin{aligned} &A \to 2Y: \quad t^+(y) = k_1 a \\ &2Y \to A \quad\; t^-(y) = k_2 y(y-1)\,. \end{aligned} \tag{7.5.26}$$

In this case, the conservation law is now simply that y is always even, or always odd. The stationary solution is of the form

$$P_s(y) = \frac{\alpha^y}{y!}\psi(y, \alpha) \tag{7.5.27}$$

where $\psi(y, \alpha)$ is a function which depends on y only through the evenness or oddness of y.

7.5.2 Stationary Solutions Without Detailed Balance (Kirchoff's Solution)

There is a method which, in principle, determines stationary solutions in general, though it does not seem to have found great practical use. The interested reader is referred to *Haken* [Ref. 7.8, Sect.4.8] and *Schnakenberg* [7.4] for a detailed treatment. In general, however, approximation methods have more to offer.

7.5.3 System Size Expansion and Related Expansions

In general we find that in chemical Master equations a system size expansion does exist. The rate of production or absorption is expected to be proportional to Ω, the size of the system. This means that as $\Omega \to \infty$, we expect

$$\boldsymbol{x} \sim \Omega\boldsymbol{\rho}\,, \tag{7.5.28}$$

where $\boldsymbol{\rho}$ is the set of chemical concentrations. Thus, we must have $t_A^{\pm}(\boldsymbol{x})$ proportional to Ω as $\Omega \to \infty$, so that this requires

$$\boxed{\begin{aligned} k_A^+ &\sim \kappa_A^+\,\Omega^{-\sum_a N_a^A+1} \\ k_A^- &\sim \kappa_A^-\,\Omega^{-\sum_a M_a^A+1}\,. \end{aligned}} \tag{7.5.29}$$

Under these circumstances, a multivariate form of van Kampen's system size expansion can be developed. This is so complicated that it will not be explicitly derived here, but as in the single variable case, we have a Kramers-Moyal expansion whose first two terms give a diffusion process whose asymptotic form is the same as that arising from a system size expansion.

The Kramers-Moyal expansion from (7.5.9) can be derived in exactly the same way as in Sect.7.2.2, in fact, rather more easily, since (7.5.9) is already in the appropriate form. Thus, we have

$$\partial_t P(\boldsymbol{x}, t) = \sum_{A,n}\left\{\frac{(\boldsymbol{r}^A\cdot\nabla)^n}{n!}[t_A^-(\boldsymbol{x})P(\boldsymbol{x}, t)] + \frac{(-\boldsymbol{r}^A\cdot\nabla)^n}{n!}[t_A^+(\boldsymbol{x})P(\boldsymbol{x}, t)]\right\} \tag{7.5.30}$$

and we now truncate this to second order to obtain

$$\boxed{\begin{aligned} &\partial_t P(\boldsymbol{x}, t) = -\sum_a \partial_a[A_a(\boldsymbol{x})P(\boldsymbol{x}, t)] + \tfrac{1}{2}\sum_{a,b}\partial_a\partial_b[B_{ab}(\boldsymbol{x})P(\boldsymbol{x}, t)]\,, && (7.5.31) \\ &\left.\begin{aligned} A_a(\boldsymbol{x}) &= \sum_A r_a^A[t_A^+(\boldsymbol{x}) - t_A^-(\boldsymbol{x})] \\ B_{ab}(\boldsymbol{x}) &= \sum_A r_a^A r_b^A[t_A^+(\boldsymbol{x}) + t_A^-(\boldsymbol{x})]\,. \end{aligned}\right\} && (7.5.32) \end{aligned}}$$

In this form we have the *chemical Fokker-Planck equation* corresponding to the Master equation. However, we note that this is really only valid as an approximation, whose large volume asymptotic expansion is identical to order $1/\Omega$ with that of the corresponding Master equation.

If one is satisfied with this degree of approximation, it is often simpler to use the Fokker-Planck equation than the Master equation.

7.6 Some Examples

7.6.1 $X + A \rightleftharpoons 2X$

Here,

$$t^+(x) = k_1 ax \qquad (7.6.1)$$
$$t^-(x) = k_2 x(x-1)\ .$$

Hence,

$$A(x) = k_1 ax - k_2 x(x-1) \sim k_1 ax - k_2 x^2 \quad \text{to order } 1/\Omega \qquad (7.6.2)$$
$$B(x) = k_1 ax + k_2 x(x-1) \sim k_1 ax + k_2 x^2 \quad \text{to order } 1/\Omega\ .$$

7.6.2 $X \underset{k}{\overset{\gamma}{\rightleftharpoons}} Y \underset{\gamma}{\overset{k}{\rightleftharpoons}} A$

Here we have

$$\left.\begin{aligned} t_1^+(\boldsymbol{x}) &= \gamma y \\ t_1^-(\boldsymbol{x}) &= kx \end{aligned}\right\} \qquad \boldsymbol{r}^1 = (1, -1) \qquad (7.6.3)$$

$$\left.\begin{aligned} t_2^+(\boldsymbol{x}) &= ka \\ t_2^-(\boldsymbol{x}) &= \gamma y \end{aligned}\right\} \qquad \boldsymbol{r}^2 = (0, 1)\ . \qquad (7.6.4)$$

Hence,

$$\boldsymbol{A}(\boldsymbol{x}) = \begin{bmatrix} 1 \\ -1 \end{bmatrix} (\gamma y - kx) + \begin{bmatrix} 0 \\ 1 \end{bmatrix} (ka - \gamma y) \qquad (7.6.5)$$

$$= \begin{bmatrix} \gamma y - kx \\ kx + ka - 2\gamma y \end{bmatrix} \qquad (7.6.6)$$

$$\underset{\sim}{\boldsymbol{B}}(\boldsymbol{x}) = \left\{\begin{bmatrix} 1 \\ -1 \end{bmatrix} (1, -1)\right\} (\gamma y + kx) + \left\{\begin{bmatrix} 0 \\ 1 \end{bmatrix} (0, 1)\right\} (ka + \gamma y) \qquad (7.6.7)$$

$$= \begin{bmatrix} \gamma y + kx & -\gamma y - kx \\ -\gamma y - kx & 2\gamma y + kx + ka \end{bmatrix}. \qquad (7.6.8)$$

If we now use the linearised form about the stationary state,

$$\gamma y = kx = ka \qquad (7.6.9)$$

$$\underset{\sim}{\boldsymbol{B}}_s = \begin{bmatrix} 2ka & -2ka \\ -2ka & 4ka \end{bmatrix}. \qquad (7.6.10)$$

7.6.3 Prey-Predator System

The prey-predator system of Sect. 1.3 provides a good example of the kind of system in which we are interested. As a chemical reaction we can write it as

$$\begin{aligned} &\text{i)}\ \ X + A \rightarrow 2X && \boldsymbol{r}^1 = (1, 0) \\ &\text{ii)}\ \ X + Y \rightarrow 2Y && \boldsymbol{r}^2 = (-1, 1) \\ &\text{iii)}\ \ Y \rightarrow B && \boldsymbol{r}^3 = (0, -1)\ . \end{aligned} \qquad (7.6.11)$$

The reactions are all irreversible (though reversibility may be introduced) so we have

$$t_A^-(\boldsymbol{x}) = 0 \qquad (A = 1, 2, 3)$$

but

$$t_1^+(\boldsymbol{x}) = k_1 a \frac{x!}{(x-1)!}\frac{y!}{y!} = k_1 ax$$
$$t_2^+(\boldsymbol{x}) = k_2 \frac{x!}{(x-1)!}\frac{y!}{(y-1)!} = k_2 xy \qquad (7.6.12)$$
$$t_3^+(\boldsymbol{x}) = k_3 \frac{x!}{x!}\frac{y!}{(y-1)!} = k_3 y\ .$$

The Master equation can now be explicitly written out using (7.5.9): one obtains

$$\partial_t P(x, y) = k_1 a(x-1)P(x-1, y) + k_2(x+1)(y-1)P(x+1, y-1)$$
$$+ k_3(y+1)\, P(x, y+1) - (k_1 ax + k_2 xy + k_3 y)\, P(x, y). \quad (7.6.13)$$

There are no exact solutions of this equation, so approximation methods must be used.

Kramers-Moyal. From (7.5.32)

$$\boldsymbol{A}(\boldsymbol{x}) = \begin{bmatrix} 1 \\ 0 \end{bmatrix} k_1 ax + \begin{bmatrix} -1 \\ 1 \end{bmatrix} k_2 xy + \begin{bmatrix} 0 \\ -1 \end{bmatrix} k_3 y \qquad (7.6.14)$$

$$= \begin{bmatrix} k_1 ax - k_2 xy \\ k_2 xy - k_3 y \end{bmatrix}, \qquad (7.6.15)$$

$$\underset{\sim}{B}(\boldsymbol{x}) = \begin{bmatrix}1\\0\end{bmatrix}(1,0)k_1ax + \begin{bmatrix}-1\\1\end{bmatrix}(-1,1)k_2xy + \begin{bmatrix}0\\-1\end{bmatrix}(0,-1)k_3y \tag{7.6.16}$$

$$= \begin{bmatrix}k_1ax + k_2xy & -k_2xy\\ -k_2xy & k_2xy + k_3y\end{bmatrix}. \tag{7.6.17}$$

The deterministic equations are

$$\frac{d}{dt}\begin{bmatrix}x\\y\end{bmatrix} = \begin{bmatrix}k_1ax - k_2xy\\ k_2xy - k_3y\end{bmatrix}. \tag{7.6.18}$$

Stationary State at

$$\begin{bmatrix}x_s\\y_s\end{bmatrix} = \begin{bmatrix}k_3/k_2\\ k_1a/k_2\end{bmatrix}. \tag{7.6.19}$$

To determine the stability of this state, we check the stability of the linearised deterministic equation

$$\frac{d}{dt}\begin{bmatrix}\delta x\\ \delta y\end{bmatrix} = \frac{\partial \boldsymbol{A}(\boldsymbol{x}_s)}{\partial x_s}\delta x + \frac{\partial \boldsymbol{A}(\boldsymbol{x}_s)}{\partial y_s}\delta y$$

$$= \begin{bmatrix}k_1a - k_2y_s\\ k_2y_s\end{bmatrix}\delta x + \begin{bmatrix}-k_2x_s\\ k_2x_s - k_3\end{bmatrix}\delta y \tag{7.6.20}$$

$$= \begin{bmatrix}0 & -k_3\\ k_1a & 0\end{bmatrix}\begin{bmatrix}\delta x\\ \delta y\end{bmatrix}. \tag{7.6.21}$$

The eigenvalues of the matrix are

$$\lambda = \pm\, \mathrm{i}(k_1k_3a)^{1/2} \tag{7.6.22}$$

which indicates a periodic motion of any small deviation from the stationary state. We thus have neutral stability, since the disturbance neither grows nor decays.

This is related to the existence of a conserved quantity

$$V = k_2(x+y) - k_3\log x - k_1a\log y \tag{7.6.23}$$

which can readily be checked to satisfy $dV/dt = 0$. Thus, the system conserves V and this means that there are different circular trajectories of constant V.

Writing again

$$x = x_s + \delta x \tag{7.6.24}$$

$$y = y_s + \delta y$$

and expanding to second order, we see that

$$V = \frac{k_2^2}{2}\left(\frac{\delta x^2}{k_3^2} + \frac{\delta y^2}{(k_1a)^2}\right) \tag{7.6.25}$$

so that the orbits are initially elliptical (this can also be deduced from the linearised analysis).

As the orbits become larger, they become less elliptic and eventually either x or y may become zero.

If x is the first to become zero (all the prey have been eaten), one sees that y inevitably proceeds to zero as well. If y becomes zero (all predators have starved to death), the prey grow unchecked with exponential growth.

Stochastic Behaviour. Because of the conservation of the quantity V, the orbits have neutral stability which means that when the fluctuations are included, the system will tend to change the size of the orbit with time. We can see this directly from the equivalent stochastic differential equations

$$\begin{bmatrix}dx\\dy\end{bmatrix} = \begin{bmatrix}k_1ax - k_2xy\\ k_2xy - k_3y\end{bmatrix}dt + \underset{\sim}{C}(x,y)\begin{bmatrix}dW_1(t)\\ dW_2(t)\end{bmatrix}, \tag{7.6.26}$$

where

$$\underset{\sim}{C}(x,y)\underset{\sim}{C}(x,y)^{\mathrm{T}} = \underset{\sim}{B}(\boldsymbol{x})\,. \tag{7.6.27}$$

Then using Ito's formula

$$dV(x,y) = \frac{\partial V}{\partial x}dx + \frac{\partial V}{\partial y}dy + \frac{1}{2}\left(\frac{\partial^2 V}{\partial x^2}dx^2 + 2\frac{\partial^2 V}{\partial x\partial y}dx\,dy + \frac{\partial^2 V}{\partial y^2}dy\right) \tag{7.6.28}$$

so that

$$\langle dV(x,y)\rangle = \left\langle \frac{\partial V}{\partial x}(k_1ax - k_2xy) + \frac{\partial V}{\partial y}(k_2xy - k_3y)\right\rangle dt \tag{7.6.29}$$

$$+ \left\langle B_{11}\frac{k_3}{2x^2} + B_{22}\frac{k_1}{2y^2}\right\rangle dt\,.$$

The first average vanishes since V is deterministically conserved and we find

$$\langle dV(x,y)\rangle = \frac{1}{2}\left\langle \frac{k_3k_1a}{x} + \frac{k_3k_2y}{x} + \frac{k_1k_2ax}{y} + \frac{k_1k_3a}{y}\right\rangle. \tag{7.6.30}$$

All of these terms are of order Ω^{-1} and are positive when x and y are positive. Thus, in the mean, $V(x,y)$ increases steadily. Of course, eventually one or other of the axes is hit and similar effects occur to the deterministic case. We see that when x or y vanish, $V = \infty$.

Direct implementation of the system size expansion is very cumbersome in this case, and moment equations prove more useful. These can be derived directly from the Master equation or from the Fokker-Planck equation. The results differ slightly from each other, by terms of order inverse volume. For simplicity, we use the FPE so that

$$\frac{d}{dt}\begin{bmatrix}\langle x\rangle\\ \langle y\rangle\end{bmatrix}=\begin{bmatrix}k_1a\langle x\rangle-k_2\langle xy\rangle\\ k_2\langle xy\rangle-k_3\langle y\rangle\end{bmatrix} \tag{7.6.31}$$

$$\frac{d}{dt}\begin{bmatrix}\langle x^2\rangle\\ \langle xy\rangle\\ \langle y^2\rangle\end{bmatrix}=\frac{1}{dt}\begin{bmatrix}\langle 2x\,dx+dx^2\rangle\\ \langle x\,dy+y\,dx+dx\,dy\rangle\\ \langle 2y\,dy+dy^2\rangle\end{bmatrix} \tag{7.6.32}$$

$$=\begin{bmatrix}2k_1a\langle x^2\rangle-2k_2\langle x^2y\rangle+k_1a\langle x\rangle+k_2\langle xy\rangle\\ k_2\langle x^2y-y^2x\rangle+(k_1a-k_3-k_2)\langle xy\rangle\\ 2k_2\langle xy^2\rangle-2k_3\langle y^2\rangle+k_2\langle xy\rangle+k_3\langle y\rangle\end{bmatrix}. \tag{7.6.33}$$

Knowing a system size expansion is valid means that we know all correlations and variances are of order $1/\Omega$ compared with the means.

We therefore write

$$\begin{aligned}x&=\langle x\rangle+\delta x\\ y&=\langle y\rangle+\delta y\end{aligned} \tag{7.6.34}$$

and keep terms only of lowest order. Noting that terms arising from $\langle dx^2\rangle$, $\langle dxdy\rangle$ and $\langle dy^2\rangle$ are one order in Ω smaller than the others, we get

$$\frac{d}{dt}\begin{bmatrix}\langle x\rangle\\ \langle y\rangle\end{bmatrix}=\begin{bmatrix}k_1a\langle x\rangle-k_2\langle x\rangle\langle y\rangle\\ k_2\langle x\rangle\langle y\rangle-k_3\langle x\rangle\langle y\rangle\end{bmatrix}+\begin{bmatrix}-k_2\langle\delta x\delta y\rangle\\ k_2\langle\delta x\delta y\rangle\end{bmatrix} \tag{7.6.35}$$

$$\begin{aligned}\frac{d}{dt}\begin{bmatrix}\langle\delta x^2\rangle\\ \langle\delta x\delta y\rangle\\ \langle\delta y^2\rangle\end{bmatrix}&=\begin{bmatrix}k_1a\langle x\rangle+k_2\langle x\rangle\langle y\rangle\\ -k_2\langle x\rangle\langle y\rangle\\ k_2\langle x\rangle\langle y\rangle+k_3\langle y\rangle\end{bmatrix}\\ &+\begin{bmatrix}2k_1a-2k_2\langle y\rangle, & -2k_2\langle x\rangle & ,\ 0\\ k_2\langle y\rangle & ,\ k_1a-k_3+k_2(\langle x\rangle-\langle y\rangle), & -k_2\langle x\rangle\\ 0 & ,\ 2k_2\langle y\rangle & ,\ 2k_2\langle x\rangle-2k_3\end{bmatrix}\begin{bmatrix}\langle\delta x^2\rangle\\ \langle\delta x\delta y\rangle\\ \langle\delta y^2\rangle\end{bmatrix}\end{aligned} \tag{7.6.36}$$

We note that the means, to lowest order, obey the deterministic equations, but to next order, the term containing $\langle\delta x\delta y\rangle$ will contribute. Thus, let us choose a simplified case in which

$$k_1a=k_3=1,\quad k_2=\alpha \tag{7.6.37}$$

which can always be done by rescaling variables. Also abbreviating

$$\langle x\rangle\to x,\ \langle y\rangle\to y,\ \langle\delta x^2\rangle\to f,\ \langle\delta x\delta y\rangle\to g,\ \langle\delta y^2\rangle\to h\,, \tag{7.6.38}$$

we obtain

$$\begin{aligned}\frac{d}{dt}\begin{bmatrix}x\\ y\end{bmatrix}&=\begin{bmatrix}x-\alpha xy\\ \alpha xy-y\end{bmatrix}+\begin{bmatrix}-\alpha g\\ \alpha g\end{bmatrix}\\ \frac{d}{dt}\begin{bmatrix}f\\ g\\ h\end{bmatrix}&=\begin{bmatrix}x+\alpha xy\\ -\alpha xy\\ \alpha xy+y\end{bmatrix}+\begin{bmatrix}2-2\alpha y & -2\alpha x & 0\\ \alpha y & \alpha(x-y) & -\alpha x\\ 0 & 2\alpha y & 2\alpha x-2\end{bmatrix}\begin{bmatrix}f\\ g\\ h\end{bmatrix}.\end{aligned} \tag{7.6.39}$$

We can attempt to solve these equations in a stationary state. Bearing in mind that f, g, h, are a factor Ω^{-1} smaller than x and y, this requires α to be of order Ω^{-1} [this also follows from the scaling requirements (7.5.29)]. Hence α is small. To lowest order one has

$$x_s=y_s=1/\alpha\,. \tag{7.6.40}$$

But the equations for f, g, h in the stationary state then become

$$\begin{bmatrix}2g\\ h-f\\ -2g\end{bmatrix}=\begin{bmatrix}2/\alpha\\ -1/\alpha\\ 2/\alpha\end{bmatrix} \tag{7.6.41}$$

which are inconsistent. Thus this method does not yield a stationary state. Alternatively one can solve all of (7.6.39) in a stationary state.

After some manipulation one finds

$$\begin{aligned}x_s&=y_s\\ g_s&=\alpha^{-1}(x_s-\alpha x_s^2)\end{aligned} \tag{7.6.42}$$

so that

$$\begin{aligned}f_s&=x_s(-2\alpha x_s^2+x_s(2-\alpha)-1)/(2-2\alpha x_s)\\ h_s&=x_s(-2\alpha x_s^2+x_s(2+\alpha)+1)/(2-2\alpha x_s)\end{aligned} \tag{7.6.43}$$

and the equation for g_s gives

$$-\alpha x_s^2+\alpha x_s(f_s-h_s)=0 \tag{7.6.44}$$

giving a solution for x_s, y_s, etc.

$$\left.\begin{aligned}x_s&=y_s=\tfrac{1}{2}\\ f_s&=\tfrac{1}{2}\alpha/(\alpha-2)\\ g_s&=\tfrac{1}{4}(2-\alpha)/\alpha\\ h_s&=-1/(\alpha-2)\end{aligned}\right\} \tag{7.6.45}$$

and for small α in which the method is valid, this leads to a negative value for f_s, which is by definition, postive. Thus there is no stationary solution.

By again approximating $x_s = y_s = 1/\alpha$, the differential equations for f, g, and h can easily be solved. We find, on assuming that initially the system has zero variances and correlations,

$$\begin{aligned} f(t) &= \frac{1}{2\alpha}(\cos 2t - 1) + \frac{2t}{\alpha} \\ g(t) &= -\frac{1}{2\alpha}\sin 2t \\ h(t) &= -\frac{1}{2\alpha}(\cos 2t - 1) + \frac{2t}{\alpha}\,. \end{aligned} \tag{7.6.46}$$

Notice that $f(t)$ and $h(t)$ are, in fact, always positive and increase steadily. The solution is valid only for a short time since the increasing value of $g(t)$ will eventually generate a time-dependent mean.

7.6.4 Generating Function Equations

In the case of combinatorial kinetics, a relatively simple differential equation can be derived for the generating function:

$$G(\boldsymbol{s},t) = \sum_{x} \left(\prod_{a} s_a^{x_a}\right) P(\boldsymbol{x},t)\,. \tag{7.6.47}$$

For we note that

$$\partial_t G(\boldsymbol{s},t) = \partial_t^+ G(\boldsymbol{s},t) + \partial_t^- G(\boldsymbol{s},t) \tag{7.6.48}$$

where the two terms correspond to the t^+ and t^- parts of the master equation. Thus

$$\begin{aligned} \partial_t^+ G(\boldsymbol{s},t) = \sum_{A,x} k_A^+ \Bigg\{ &\prod_a \left[\frac{(x_a - r_a^A)!}{(x_a - r_a^A - N_a^A)!} s_a^{x_a}\right] P(\boldsymbol{x} - \boldsymbol{r}^A, t) \\ &- \prod_a \left[\frac{x_a!}{(x_a - N_a^A)!} s_a^{x_a}\right] P(\boldsymbol{x},t) \Bigg\}\,. \end{aligned} \tag{7.6.49}$$

Changing the summation variable to $\boldsymbol{x} - \boldsymbol{r}^A$ and renaming this as $\boldsymbol{x}$, in the first term we find

$$\partial_t^+ G(\boldsymbol{s},t) = \sum_{A,x} k_A^+ \left[\prod_a \frac{x_a!}{(x_a - N_a^A)!} s_a^{x_a + r_a^A} - \prod_a \frac{x_a!}{(x_a - N_a^A)!} s_a^{x_a}\right] P(\boldsymbol{x},t)\,. \tag{7.6.50}$$

Note that

$$\prod_a \frac{s_a^{x_a} x_a!}{(x_a - N_a^A)!} = \prod_a \left(\partial_a^{N_a^A} s_a^{x_a}\right) s_a^{N_a^A} \tag{7.6.51}$$

and that

$$\prod_a \frac{s_a^{x_a + r_a^A} x_a!}{(x_a - N_a^A)!} = \prod_a \left(\partial_a^{N_a^A} s_a^{x_a}\right) s_a^{M_a^A} \tag{7.6.52}$$

so that

$$\partial_t^+ G(\boldsymbol{s},t) = \sum_A k_A^+ \left(\prod_a s_a^{M_a^A} - \prod_a s_a^{N_a^A}\right) \partial_a^{N_a^A} G(\boldsymbol{s},t)\,. \tag{7.6.53}$$

Similarly, we derive a formula for $\partial_t^- G(\boldsymbol{s},t)$ and put these together to get

$$\boxed{\partial_t G(\boldsymbol{s},t) = \sum_A \left(\prod_a s_a^{M_a^A} - \prod_a s_a^{N_a^A}\right) \left(k_A^+ \prod_a \partial_a^{N_a^A} - k_A^- \prod_a \partial_a^{M_a^A}\right) G(\boldsymbol{s},t)} \tag{7.6.54}$$

which is the general formula for a generating function differential equation. We now give a few examples.

a) An Exactly Soluble Model
Reactions: (A, B, C held fixed)

$$\begin{aligned} &A + X \xrightarrow{k_2} 2X + D \qquad && N^1 = 1,\ M^1 = 2;\ r^1 = 1 \\ &&& k_1^+ = k_2 A \\ &&& k_1^- = 0 \end{aligned} \tag{7.6.55}$$

$$\begin{aligned} &B + X \underset{k_3}{\overset{k_1}{\rightleftharpoons}} C \qquad && N^2 = 1,\ M^2 = 0;\ r^2 = -1 \\ &&& k_2^+ = k_1 B \\ &&& k_2^- = k_3 C\,. \end{aligned} \tag{7.6.56}$$

Hence, from (7.6.54), the generating function equation is

$$\partial_t G = (s^2 - s)(k_2 A \partial_s G) + (1 - s)(k_1 B \partial_s G - k_3 C G)\,. \tag{7.6.57}$$

Solve by characteristics.
Set

$$k_1 B = \beta, \qquad k_2 A = \alpha, \qquad k_3 C = \gamma\,. \tag{7.6.58}$$

The characteristics are

$$\frac{dt}{1} = -\frac{ds}{(1-s)(\beta - \alpha s)} = \frac{dG}{\gamma(1-s)G} \tag{7.6.59}$$

. . .

$$\left(\frac{1-s}{\beta-\alpha s}\right)\mathrm{e}^{(\alpha-\beta)t}=u \tag{7.6.60}$$

$$(\beta-\alpha s)^{\gamma/\alpha}G=v\,. \tag{7.6.61}$$

The general solution can be written $v=F(u)$, i.e.,

$$G=(\beta-\alpha s)^{-\gamma/\alpha}F\left\{\mathrm{e}^{(\alpha-\beta)t}\left(\frac{1-s}{\beta-\alpha s}\right)\right\}. \tag{7.6.62}$$

From this we can find various time-dependent solutions. The conditional probability $P(x,t\,|\,y,0)$ comes from the initial condition

$$G_y(s,0)=s^y \tag{7.6.63}$$

$$\Rightarrow F(z)=(1-\beta z)^y(1-\alpha z)^{-\gamma/\alpha-y}(\beta-\alpha)^{\gamma/\alpha} \tag{7.6.64}$$

$$\boxed{\begin{aligned}\Rightarrow G_y(s,t)&=\lambda^{\gamma/\alpha}[\beta(1-\mathrm{e}^{-\lambda t})-s(\alpha-\beta\mathrm{e}^{-\lambda t})]^y\\ &\quad\times[(\beta-\alpha\mathrm{e}^{-\lambda t})-\alpha s(1-\mathrm{e}^{-\lambda t})]^{-\gamma/\alpha-y}\end{aligned}} \tag{7.6.65}$$

(with $\lambda=\beta-\alpha$).

As $t\to\infty$, a stationary state exists only if $\beta>\alpha$ and is

$$G_y(s,\infty)=(\beta-\alpha s)^{-\gamma/\alpha}(\beta-\alpha)^{\gamma/\alpha} \tag{7.6.66}$$

$$\Rightarrow P_s(x)=\frac{\Gamma(x+\gamma/\alpha)(\alpha/\beta)^x}{\Gamma(\gamma/\alpha)x!}(\beta-\alpha)^{\gamma/\alpha}\,. \tag{7.6.67}$$

We can also derive moment equations from the generating function equations by noting

$$\begin{aligned}\partial_s G(s,t)|_{s=1}&=\langle x(t)\rangle\\ \partial_s^2 G(s,t)|_{s=1}&=\langle x(t)[x(t)-1]\rangle\,.\end{aligned} \tag{7.6.68}$$

Proceeding this way we have

$$\frac{d}{dt}\langle x(t)\rangle=(k_2A-k_1B)\langle x(t)\rangle+k_3C \tag{7.6.69}$$

and

$$\begin{aligned}\frac{d}{dt}\langle x(t)[x(t)-1]\rangle&=2(k_2A-k_1B)\langle x(t)[x(t)-1]\rangle\\ &\quad+2k_2A\langle x(t)\rangle+2k_3C\langle x(t)\rangle\,.\end{aligned} \tag{7.6.70}$$

These equations have a stable stationary solution provided

$$k_2A<k_1B,\qquad \text{i.e.,}\quad \alpha<\beta\,.$$

In this case, the stationary mean and variance are

$$\langle x\rangle_s=k_3C/(k_1B-k_2A) \tag{7.6.71}$$

$$\operatorname{var}\{x\}_s=k_1k_3BC/(k_2A-k_1B)^2\,. \tag{7.6.72}$$

This model is a simple representation of the processes taking place in a nuclear reactor. Here X is a neutron. The first reaction represents the fission by absorption of a neutron by A to produce residue(s) D plus two neutrons. The second represents absorption of neutrons and production by means other than fission.

As k_2A approaches k_1B, we approach a critical situation where neutrons are absorbed and created in almost equal numbers. For $k_2A>k_1B$, an explosive chain reaction occurs. Notice that $\langle x_s\rangle$ and $\operatorname{var}\{x\}_s$ both become very large as a critical point is approached and, in fact,

$$\frac{\operatorname{var}\{x_s\}}{\langle x\rangle_s}=\frac{k_1B}{k_1B-k_2A}\to\infty\,. \tag{7.6.73}$$

Thus, there are *very* large fluctuations in $\langle x_s\rangle$ near the critical point.

Note also that the system has linear equations for the mean and is Markovian, so the methods of Sect. 3.7.4 (the regression theorem) show that

$$\langle x(t),x(0)\rangle_s=\exp[(k_2A-k_1B)t]\operatorname{var}\{x\}_s \tag{7.6.74}$$

so that the fluctuations become vanishingly slow as the critical point is approached, i.e., the time correlation function decays very slowly with time.

b) Chemical Reaction $X_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X_2$

One reaction

$$\begin{aligned}&N=\begin{bmatrix}1\\0\end{bmatrix},\qquad M=\begin{bmatrix}0\\1\end{bmatrix},\qquad r=\begin{bmatrix}-1\\1\end{bmatrix}\\ &k_1^+=k_1,\qquad k_1^-=k_2\\ &\partial_t G(s_1,s_2,t)=(s_2-s_1)(k_1\partial_{s_1}-k_2\partial_{s_2})G(s_1,s_2,t)\end{aligned} \tag{7.6.75}$$

can be solved by characteristics. The generating function is an arbitrary function of solutions of

$$\frac{dt}{1}=-\frac{ds_1}{k_1(s_2-s_1)}=\frac{ds_2}{k_2(s_2-s_1)}\,. \tag{7.6.76}$$

Two integrals are solutions of

$$k_2ds_1+k_1ds_2=0\Longrightarrow k_2s_1+k_1s_2=v\,. \tag{7.6.77}$$

$$(k_1 + k_2)dt = \frac{d(s_2 - s_1)}{s_2 - s_1} \qquad (7.6.78)$$
$$\Longrightarrow (s_2 - s_1)e^{-(k_1+k_2)t} = u$$

$$\therefore\ G(s_1, s_2, t) = F[k_2 s_1 + k_1 s_2, (s_2 - s_1)e^{-(k_1+k_2)t}] \,. \qquad (7.6.79)$$

The initial condition (Poissonian)

$$G(s_1, s_2, 0) = \exp[\alpha(s_1 - 1) + \beta(s_2 - 1)] \qquad (7.6.80)$$

gives the Poissonian solution:

$$G(s_1, s_2, t) = \exp\left\{\frac{k_2\beta - k_1\alpha}{k_1 + k_2}(s_2 - s_1)e^{-(k_1+k_2)t} + \frac{\alpha + \beta}{k_1 + k_2}[k_1(s_2 - 1) + k_2(s_1 - 1)]\right\}. \qquad (7.6.81)$$

In this case, the stationary solution is not unique because $x + y$ is a conserved quantity. From (7.6.79) we see that the general stationary solution is of the form

$$G(s_1, s_2, \infty) = F(k_2 s_1 + k_1 s_2, 0) \,. \qquad (7.6.82)$$

Thus,

$$k_1^n \frac{\partial^n G}{\partial s_1^n} = k_2^n \frac{\partial^n G}{\partial s_2^n} \qquad (7.6.83)$$

which implies that, setting $s_1 = s_2 = 1$,

$$k_1^n \langle x_1^n \rangle_f = k_2^n \langle x_2^n \rangle_f \,. \qquad (7.6.84)$$

7.7 The Poisson Representation [7.10]

This is a particularly elegant technique which generates Fokker-Planck equations which are equivalent to chemical Master equations of the form (7.5.9).

We *assume* that we can expand $P(\boldsymbol{x}, t)$ as a superposition of multivariate uncorrelated Poissons:

$$P(\boldsymbol{x}, t) = \int d\boldsymbol{\alpha} \prod_a \frac{e^{-\alpha_a}\alpha_a^{x_a}}{x_a!} f(\boldsymbol{\alpha}, t) \,. \qquad (7.7.1)$$

This means that the generating function $G(\boldsymbol{s}, t)$ can be written

$$G(\boldsymbol{s}, t) = \int d\boldsymbol{\alpha}\ \exp\left[\sum_a (s_a - 1)\alpha_a\right] f(\boldsymbol{\alpha}, t) \,. \qquad (7.7.2)$$

We substitute this in the generating function equation (7.6.54) to get

$$\partial_t G(\boldsymbol{s}, t) = \sum_A \int d\boldsymbol{\alpha} \left\{\left[\prod_a \left(\frac{\partial}{\partial \alpha_a} + 1\right)^{M_a^A} - \prod_a \left(\frac{\partial}{\partial \alpha_a} + 1\right)^{N_a^A}\right] \times \left(k_A^+ \prod_a \alpha_a^{N_a^A} - k_A^- \prod_a \alpha_a^{M_a^A}\right) \exp\left[\sum_a (s_a - 1)\alpha_a\right]\right\} f(\boldsymbol{\alpha}, t) \,. \qquad (7.7.3)$$

We now integrate by parts, drop surface terms and finally equate coefficients of the exponential to obtain

$$\boxed{\frac{\partial f(\boldsymbol{\alpha}, t)}{\partial t} = \sum_A \left[\prod_a \left(1 - \frac{\partial}{\partial \alpha_a}\right)^{M_a^A} - \prod_a \left(1 - \frac{\partial}{\partial \alpha_a}\right)^{N_a^A}\right] \times \left[k_A^+ \prod_a \alpha_a^{N_a^A} - k_A^- \prod_a \alpha_a^{M_a^A}\right] f(\boldsymbol{\alpha}, t) \,.} \qquad (7.7.4)$$

a) Fokker-Planck Equations for Bimolecular Reaction Systems

This equation is of the Fokker-Planck form if we have, as is usual in real chemical reactions,

$$\sum_a M_a^A \leqslant 2$$
$$\sum_a N_a^A \leqslant 2 \qquad (7.7.5)$$

which indicates that only pairs of molecules at the most participate in reactions. The FPE can then be simplified as follows. Define the currents

$$J_A(\boldsymbol{\alpha}) = k_A^+ \prod_a \alpha_a^{N_a^A} - k_A^- \prod_a \alpha_a^{M_a^A} \,, \qquad (7.7.6)$$

the drifts

$$A_a[\boldsymbol{J}(\boldsymbol{\alpha})] = \sum_A r_a^A J_A(\boldsymbol{\alpha}) \,, \qquad (7.7.7)$$

and the diffusion matrix elements by

$$B_{ab}[\boldsymbol{J}(\boldsymbol{\alpha})] = \sum_A J_A(\boldsymbol{\alpha})(M_a^A M_b^A - N_a^A N_b^A - \delta_{a,b} r_a^A) \,. \qquad (7.7.8)$$

Then the Poisson representation FPE is

$$\boxed{\frac{\partial f(\boldsymbol{\alpha}, t)}{\partial t} = -\sum_a \frac{\partial}{\partial \alpha_a}\{A_a[\boldsymbol{J}(\boldsymbol{\alpha})] f(\boldsymbol{\alpha}, t)\} + \tfrac{1}{2}\sum_{a,b} \frac{\partial^2}{\partial \alpha_a \partial \alpha_b}\{B_{ab}[\boldsymbol{J}(\boldsymbol{\alpha})] f(\boldsymbol{\alpha}, t)\} \,.} \qquad (7.7.9)$$

Notice also that if we use the explicit volume dependence of the parameters given in Sect. 7.5.3 (7.5.29) and define

$$\eta_a = \alpha_a/V \tag{7.7.10}$$

$$\varepsilon = V^{-1/2} \tag{7.7.11}$$

and $F(\boldsymbol{\eta}, t)$ is the quasiprobability in the η variable, then the FPE for the η variable takes the form of

$$\frac{\partial F(\boldsymbol{\eta}, t)}{\partial t} = -\sum_a \frac{\partial}{\partial \eta_a}[\hat{A}_a(\boldsymbol{\eta})F(\boldsymbol{\eta}, t)] + \frac{\varepsilon^2}{2}\sum_{a,b}\frac{\partial^2}{\partial\eta_a\partial\eta_b}[\hat{B}_{a,b}(\boldsymbol{\eta})F(\boldsymbol{\eta}, t)] \tag{7.7.12}$$

with

$$\hat{A}_a(\boldsymbol{\eta}) = \sum_A r_a^A \hat{J}_A(\eta) \tag{7.7.13a}$$

$$\hat{J}_A(\eta) = \kappa_A^+ \prod_a \eta_a^{N_a^A} - \kappa_A^- \prod_a \eta_a^{M_a^A} \tag{7.7.13b}$$

$$\hat{B}_{ab}(\boldsymbol{\eta}) = \sum_A \hat{J}_A(\boldsymbol{\eta})(M_a^A M_b^A - N_a^A N_b^A - \delta_{a,b} r_a^A)\,. \tag{7.7.13c}$$

In this form we see how the system size expansion in $V^{-1/2}$ corresponds exactly to a small noise expansion in η of the FPE (7.7.12). For such birth-death Master equations, this method is technically much simpler than a direct system size expansion.

b) Unimolecular Reactions

If for all A,

$$\sum_a M_a^A \leqslant 1 \qquad \text{and} \qquad \sum_a N_a^A \leqslant 1,$$

then it is easily checked that the diffusion coefficient $\hat{B}_{ab}(\boldsymbol{\eta})$ in (7.7.13) vanishes, and we have a Liouville equation. An initially Poissonian $P(\boldsymbol{x}, t_0)$, corresponds to a delta function $F(\boldsymbol{\eta}, t_0)$, and the time evolution generated by this Liouville equation will generate a delta function solution, $\delta(\boldsymbol{\eta} - \bar{\boldsymbol{\eta}}(t))$, where $\bar{\boldsymbol{\eta}}(t)$ is the solution of

$$d\boldsymbol{\eta}/dt = \boldsymbol{A}(\boldsymbol{\eta})$$

This means that $P(\boldsymbol{x}, t)$ will preserve a Poissonian form, with mean equal to $\bar{\boldsymbol{\eta}}(t)$. Thus we derive the general result, that there exist propagating multipoissonian solutions for any unimolecular reaction system. Non Poissonian solutions also exist—these correspond to initial $F(\boldsymbol{\eta}, t_0)$ which are not delta functions.

c) Example

As an example, consider the reaction pair

$$\begin{aligned} &\text{i)}\quad A + X \underset{k_4}{\overset{k_2}{\rightleftharpoons}} 2X \\ &\text{ii)}\quad B + X \underset{k_3}{\overset{k_1}{\rightleftharpoons}} C \end{aligned} \tag{7.7.14}$$

$$\begin{aligned} &N^1 = 1, \quad M^1 = 2, \quad k_1^+ = k_2 A, \quad k_1^- = k_4 \\ &N^2 = 1, \quad M^2 = 0, \quad k_2^+ = k_1 B, \quad k_2^- = k_3 C \end{aligned}$$

so that (7.7.4) takes the form

$$\begin{aligned} \frac{\partial f}{\partial t} = &\left[\left(1 - \frac{\partial}{\partial\alpha}\right)^2 - \left(1 - \frac{\partial}{\partial\alpha}\right)\right](k_2 A\alpha - k_4\alpha^2)f \\ &+ \left[1 - \left(1 - \frac{\partial}{\partial\alpha}\right)\right](k_1 B\alpha - k_3 C)f \end{aligned} \tag{7.7.15}$$

$$\frac{\partial f}{\partial t} = \left\{-\frac{\partial}{\partial\alpha}[k_3 C + (k_2 A - k_1 B)\alpha - k_4\alpha^2] + \frac{\partial^2}{\partial\alpha^2}[k_2 A\alpha - k_4\alpha^2]\right\} f \tag{7.7.16}$$

which is of the Fokker-Planck form, provided $k_2 A\alpha - k_4\alpha^2 > 0$. Furthermore, there is the simple relationship between moments, which takes the form (in the case of one variable)

$$\begin{aligned} \langle x^r \rangle_f &= \sum_x \int d\alpha\, [x(x-1)\dots(x-r+1)\frac{e^{-\alpha}\alpha^x}{x!}\, f(\alpha) \\ &= \int d\alpha\, \alpha^r f(\alpha) \equiv \langle \alpha^r \rangle\,. \end{aligned} \tag{7.7.17}$$

This follows from the factorial moments of the Poisson distribution (Sect. 2.8.3). However, $f(\alpha)$ is not a probability or at least, is not guaranteed to be a probability in the simple minded way it is defined. This is clear, since any positive superposition of Poisson distributions must have a variance at least as wide as the Poisson distribution. Hence any $P(\boldsymbol{x})$ for which the variance is less than that of the Poisson distribution i.e., cannot be represented by a positive $f(\boldsymbol{\alpha})$.

A representation in terms of *distributions* is always possible, at least formally. For if we define

$$f_y(\alpha) = (-1)^y \delta^y(\alpha) e^{\alpha}, \qquad \text{then} \tag{7.7.18}$$

$$\int d\alpha\, f_y(\alpha) e^{-\alpha}\alpha^x/x! = \int d\alpha\, \alpha^x \left(-\frac{d}{d\alpha}\right)^y \delta(\alpha)/x! \tag{7.7.19}$$

and integrating by parts

$$= \delta_{x,y} \tag{7.7.20}$$

which means that we can write

$$P(x) = \int d\alpha (e^{-\alpha}\alpha^x/x!)[\sum_y (-1)^y P(y)\delta^y(\alpha)e^{\alpha}] \tag{7.7.21}$$

so that in a *formal* sense, an $f(\alpha)$ can always be found for any $P(x)$.

The rather singular form just given does not, in fact, normally arise since, for example, we can find the stationary solution of the FPE (7.7.16) as the potential solution (up to a normalisation)

$$f_s(\alpha) = \mathrm{e}^{\alpha}(k_2A - k_4\alpha)^{(k_1B/k_4 - k_3C/k_2A - 1)}\alpha^{k_3C/k_2A - 1} \tag{7.7.22}$$

which is a relatively smooth function. However, an interpretation as a probability is only possible if $f_s(\alpha)$ is positive or zero and is normalisable.

If we define

$$\delta = (k_1B/k_4 - k_3C/k_2A), \tag{7.7.23}$$

then $f_s(\alpha)$ is normalisable on the interval $(0, k_2A/k_4)$ provided that

$$\begin{aligned} &\delta > 0 \\ &k_3 > 0. \end{aligned} \tag{7.7.24}$$

Clearly, by definition, k_3 must be positive.

It must further be checked that the integrations by parts used to derive the FPE (7.7.4) are such that under these conditions, surface terms vanish. For an interval (a, b) the surface terms which would arise in the case of the reaction (7.7.14) can be written

$$\begin{aligned} &[\{(k_2A\alpha - k_4\alpha^2 - k_1B\alpha + k_3C)f - \partial_\alpha[(k_2\alpha - k_4\alpha^2)f]\}\{\mathrm{e}^{(s-1)\alpha}\}]_b^a \\ &\quad + [(k_2\alpha - k_4\alpha^2)f[(s-1)\mathrm{e}^{(s-1)\alpha}]]_b^a\,. \end{aligned} \tag{7.7.25}$$

Because of the extra factor $(s - 1)$ on the second line, each line must vanish separately. It is easily checked that on the interval $(0, k_2A/k_4)$, each term vanishes at each end of the interval for the choice (7.7.22) of f, provided δ and k_3 are both greater than zero.

In the case where k_3 and δ are both positive, we have a genuine FPE equivalent to the stochastic differential equation

$$d\alpha = [k_3C + (k_2A - k_1B)\alpha - k_4\alpha^2]dt + \sqrt{2(k_2A\alpha - k_4\alpha^2)}dW(t)\,. \tag{7.7.26}$$

The motion takes place on the range $(0, k_2A/k_4)$ and both boundaries satisfy the criteria for *entrance boundaries*, which means that it is not possible to leave the range $(0, k_2A/k_4)$ (Sect. 5.2.1).

If either of the conditions (7.7.24) is violated, it is found that the drift vector is such as to take the point outside the interval $(0, k_2A/k_4)$. For example, near $\alpha = 0$ we have

$$d\alpha \sim k_3C\,dt \tag{7.7.27}$$

and if k_3C is negative, α will proceed to negative values. In this case, the coefficient of $dW(t)$ in (7.7.26) becomes imaginary and interpretation is no longer possible without further explanation.

Of course, viewed as a SDE in the *complex* variable

$$\alpha = \alpha_x + \mathrm{i}\alpha_y\,, \tag{7.7.28}$$

the SDE is perfectly sensible and is really a pair of stochastic differential equations for the two variables α_x and α_y. However, the corresponding FPE is no longer the one variable equation (7.7.16) but a two-variable FPE. We can derive such a FPE in terms of variations of the Poisson representation, which we now treat.

7.7.1 Kinds of Poisson Representations

Let us consider the case of one variable and write

$$P(x) = \int_{\mathscr{D}} d\mu(\alpha)(\mathrm{e}^{-\alpha}\alpha^x/x!)f(\alpha)\,. \tag{7.7.29}$$

Then $\mu(\alpha)$ is a measure which we will show may be chosen in three ways which all lead to useful representations, and $\mathscr{D}$ is the domain of integration, which can take on various forms, depending on the choice of measure.

7.7.2 Real Poisson Representations

Here we choose

$$d\mu(\alpha) = d\alpha \tag{7.7.30}$$

and $\mathscr{D}$ is a section of the real line. As noted in the preceding example, this representation does not always exist, but where it does, a simple interpretation in terms of Fokker-Planck equations is possible.

7.7.3 Complex Poisson Representations

Here,

$$d\mu(\alpha) = d\alpha \tag{7.7.31}$$

and $\mathscr{D}$ is a contour C in the complex plane. We can show that this exists under certain restrictive conditions. For, instead of the form (7.7.18), we can choose

$$f_y(\alpha) = \frac{y!}{2\pi\mathrm{i}}\,\alpha^{-y-1}\mathrm{e}^{\alpha} \tag{7.7.32}$$

and C to be a contour surrounding the origin. This means that

$$P_y(x) = \frac{1}{2\pi\mathrm{i}}\oint_{C}\frac{y!}{x!}\,\alpha^{x-y-1} = \delta_{x,y}\,. \tag{7.7.33}$$

By appropriate summation, we may express a given $P(x)$ in terms of an $f(\alpha)$ given by

$$f(\alpha) = \frac{1}{2\pi\mathrm{i}}\sum_y P(y)\mathrm{e}^{\alpha}\alpha^{-y-1}y!\,. \tag{7.7.34}$$

If the $P(y)$ are such that for all y, $y!P(y)$ is bounded, the series has a finite radius of convergence outside which $f(\alpha)$ is analytic. By choosing C to be outside this circle of convergence, we can take the integration inside the summation to find that $P(x)$ is given by

$$P(x) = \oint_C d\alpha (e^{-\alpha}\alpha^x/x!)f(\alpha) . \tag{7.7.35}$$

a) Example: Reactions (1) $A + X \rightleftharpoons 2X$, (2) $B + X \rightleftharpoons C$
We use the notation of Sect. 7.7 and distinguish three cases, depending on the magnitude of δ. The quantity δ gives a measure of the direction in which the reaction system (7.7.14) is proceeding when a steady state exists. If $\delta > 0$, we find that when x has its steady state value, reaction (1) is producing X while reaction (2) consumes X. When $\delta = 0$, both reactions balance separately—thus we have chemical equilibrium. When $\delta < 0$, reaction (1) consumes X while reaction (2) produces X.
i) $\delta > 0$: according to (7.7.24), this is the condition for $f_s(\alpha)$ to be a valid quasiprobability on the real interval $(0, k_2A/k_4)$. In this range, the diffusion coefficient $(k_2A\alpha - k_4\alpha^2)$ is positive. The deterministic mean of α, given by

$$\alpha = \frac{k_2A - k_1B + [(k_2A - k_1B)^2 + 4k_3k_4C]^{1/2}}{2k_4} \tag{7.7.36}$$

lies *within* the interval $(0, k_2A/k_4)$. We are therefore dealing with the case of a genuine FPE and $f_s(\alpha)$ is a function vanishing at both ends of the interval and peaked near the deterministic steady state.

ii) $\delta = 0$: since both reactions now balance separately, we expect a Poissonian steady state. We note that $f_s(\alpha)$ in this case has a pole at $\alpha = k_2A/k_4$ and we choose the range of α to be a contour in the complex plane enclosing this pole. Since this is a closed contour, there are no boundary terms arising from partial integration and $P_s(x)$ given by choosing this type of Poisson representation clearly satisfies the steady state Master equation. Now using the calculus of residues, we see that

$$P_s(x) = \frac{e^{-\alpha_0}\alpha_0^x}{x!} \tag{7.7.37}$$

with

$$\alpha_0 = k_2A/k_4 .$$

iii) $\delta < 0$: when $\delta < 0$ we meet some very interesting features. The steady state solution (7.7.22) now no longer satisfies the condition $\delta > 0$. However, if the range of α is chosen to be a contour C in the complex plane (Fig. 7.3) and we employ the complex Poisson representation, $P_s(x)$ constructed as

$$P_s(x) = \int_C d\alpha\, f_s(\alpha) \frac{e^{-\alpha}\alpha^x}{x!} \tag{7.7.38}$$

is a solution of the Master equation. The deterministic steady state now occurs at a point on the real axis to the right of the singularity at $\alpha = k_2A/k_4$, and asymptotic evaluations of means, moments, etc., may be obtained by choosing C to pass through the saddle point that occurs there. In doing so, one finds that the variance of α, defined as

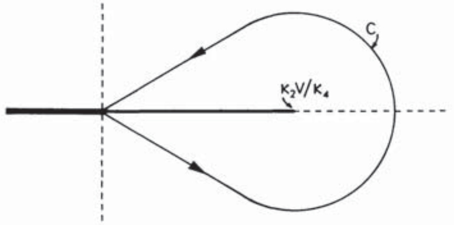

Fig. 7.3. Contour C in the complex plane for the evaluation of (7.7.38)

$$\operatorname{var}\{\alpha\} = \langle\alpha^2\rangle - \langle\alpha\rangle^2 , \tag{7.7.39}$$

is negative, so that

$$\operatorname{var}\{x\} = \langle x^2\rangle - \langle x\rangle^2 = \langle\alpha^2\rangle - \langle\alpha\rangle^2 + \langle\alpha\rangle < \langle x\rangle \tag{7.7.40}$$

This means that the steady state is narrower than the Poissonian. Finally, it should be noted that all three cases can be obtained from the contour C. In the case where $\delta = 0$, the cut from the singularity at $\alpha = k_2A/k_4$ to $-\infty$ vanishes and C may be distorted to a simple contour round the pole, while if $\delta > 0$, the singularity at $\alpha = k_2A/k_4$ is now integrable so the contour may be collapsed onto the cut and the integral evaluated as a discontinuity integral over the range $[0, k_2A/k_4]$. (When δ is a positive integer, this argument requires modification).

b) Example: Reactions $B \xrightarrow{k_1} X$, $2X \xrightarrow{k_2} A$
For which the Fokker-Planck equation is

$$\frac{\partial f(\alpha, t)}{\partial t} = -\frac{\partial}{\partial\alpha}[(\kappa_1V - 2\kappa_2V^{-1}\alpha^2)f(\alpha, t)] - \frac{\partial^2}{\partial\alpha^2}[(\kappa_2V^{-1}\alpha^2)f(\alpha, t)] , \tag{7.7.41}$$

where $\kappa_1V = k_1B$, $\kappa_2V^{-1} = k_2$ and V is the system volume. Note that the diffusion coefficient in the above FPE is negative on all the real lines.

The potential solution of (7.7.41) is (up to a normalisation factor)

$$f(\alpha) = \alpha^{-2} \exp(2\alpha + aV^2/\alpha) \tag{7.7.42}$$

with $a = 2\kappa_2/\kappa_1$ and the α integration is to be performed along a closed contour encircling the origin. Of course, in principle, there is another solution obtained by solving the stationary FPE in full. However, only the potential solution is single valued and allows us to choose an acceptable contour on which partial integration is permitted.

Thus, by putting $\alpha = \eta V$, we get

$$\langle x^r\rangle_f = \frac{V^r \oint d\eta\, e^{V(2\eta + a/\eta)}\eta^{r-2}}{\oint d\eta\, e^{V(2\eta + a/\eta)}\eta^{-2}} . \tag{7.7.43}$$

The function $(2\eta + a/\eta)$ does not have a maximum at the deterministic steady state. In fact, it has a minimum at the deterministic steady state $\eta = +(a/2)^{1/2}$.

However, in the complex η plane this point is a saddle point and provides the dominant contribution to the integral.

Thus, the negative diffusion coefficient in (7.7.41) reflects itself by giving rise to a saddle point at the deterministic steady state, which results in the variance in X being less than $\langle x\rangle$.

From (7.7.43) all the steady states moments can be calculated exactly. The results are

$$\langle x^r\rangle_f = \left[V\left(\frac{a}{2}\right)^{1/2}\right]^r \frac{\mathrm{I}_{r-1}(2(2a)^{1/2}V)}{\mathrm{I}_1(2(2a)^{1/2}V)}\,, \tag{7.7.44}$$

where $\mathrm{I}_r(2(2a)^{1/2}V)$ are the modified Bessel functions. Using the large-argument expansion for $\mathrm{I}_r(2(2a)^{1/2}V)$, we get

$$\begin{aligned}&\langle x\rangle = V(a/2)^{1/2} + \tfrac{1}{8} + O(1/V)\\ &\operatorname{var}\{x\} = \tfrac{3}{4}\,V(a/2)^{1/2} - \tfrac{1}{16} + O(1/V)\,.\end{aligned} \tag{7.7.45}$$

These asymptotic results can also be obtained by directly applying the method of steepest descents to (7.7.43). In general, this kind of expansion will always be possible after explicitly exhibiting the volume dependence of the parameters.

c) Summary of Advantages

The complex Poisson representation yields stationary solutions in analytic form to which asymptotic or exact methods are easily applicable. It is not so useful in the case of time-dependent solutions. The greatest advantages, however, occur in quantum mechanical systems where similar techniques can be used for complex P representations which can give information that is not otherwise extractable. These are treated in Chap. 10.

7.7.4 The Positive Poisson Representation

Here we choose α to be a complex variable $\alpha_x + \mathrm{i}\alpha_y$,

$$d\mu(\alpha) = d^2\alpha = d\alpha_x d\alpha_y\,, \tag{7.7.46}$$

and $\mathscr{D}$ is the whole complex plane. We show in Sect. 10.6.3 that *for any $P(x)$, a positive $f(\alpha)$ exists such that*

$$P(x) = \int d^2\alpha\,(\mathrm{e}^{-\alpha}\alpha^x/x!)f(\alpha)\,; \tag{7.7.47}$$

thus, the positive P representation always exists. It is not unique, however. For example, choose

$$f_p(\alpha) = (2\pi\sigma^2)^{-1}\exp\left(-|\alpha-\alpha_0|^2/2\sigma^2\right) \tag{7.7.48}$$

and note that if $g(\alpha)$ is any analytic function of α, we can write

$$g(\alpha) = g(\alpha_0) + \sum_{n=1}^{\infty} g^{(n)}(\alpha_0)(\alpha-\alpha_0)^n/n! \tag{7.7.49}$$

so that

$$\int (2\pi\sigma^2)^{-1}d^2\alpha\exp\left(-|\alpha-\alpha_0|^2/2\sigma^2\right)g(\alpha) = g(\alpha_0)\,, \tag{7.7.50}$$

since the terms with $n \geqslant 1$ vanish when integrated in (7.7.50). Noting that the Poisson form $\mathrm{e}^{-\alpha}\alpha^x/x!$ is itself analytic in α, we obtain for any positive value of σ^2

$$P(x) = \int d^2\alpha\, f_p(\alpha)\mathrm{e}^{-\alpha}\alpha^x/x! = \mathrm{e}^{-\alpha_0}\alpha_0^x/x!\,. \tag{7.7.51}$$

In practice, this nonuniqueness is an advantage rather than a problem.

a) Fokker-Planck Equations

We make use of the analyticity of the Poisson and its generating function to produce Fokker-Planck equations with positive diffusion matrices. A FPE of the form of (7.7.9) arises from a generating function equation

$$\partial_t G(\boldsymbol{s},t) = \int d^2\boldsymbol{\alpha}\, f(\boldsymbol{\alpha},t)\left(\sum_a A_a\frac{\partial}{\partial\alpha_a} + \sum_{a,b}\tfrac{1}{2}B_{ab}\frac{\partial^2}{\partial\alpha_a\partial\alpha_b}\right)\exp\left[\sum_a(s_a-1)\alpha_a\right]. \tag{7.7.52}$$

We now take explicit account of the fact that $\boldsymbol{\alpha}$ is a complex variable

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}_x + \mathrm{i}\boldsymbol{\alpha}_y \tag{7.7.53}$$

and also write

$$\boldsymbol{A}(\boldsymbol{\alpha}) = \boldsymbol{A}_x(\boldsymbol{\alpha}) + \mathrm{i}\boldsymbol{A}_y(\boldsymbol{\alpha})\,. \tag{7.7.54}$$

We further write

$$\underline{B}(\boldsymbol{\alpha}) = \underline{C}(\boldsymbol{\alpha})\underline{C}^{\mathrm{T}}(\boldsymbol{\alpha}) \tag{7.7.55}$$

and

$$\underline{C}(\boldsymbol{\alpha}) = \underline{C}_x(\boldsymbol{\alpha}) + \mathrm{i}\underline{C}_y(\boldsymbol{\alpha}) \tag{7.7.56}$$

For brevity we use

$$\begin{aligned}\partial_a &= \frac{\partial}{\partial\alpha_a}\\ \partial_a^x &= \frac{\partial}{\partial\alpha_{x,a}}\\ \partial_a^y &= \frac{\partial}{\partial\alpha_{y,a}}\,.\end{aligned} \tag{7.7.57}$$

Because of the analyticity of $\exp\left[\sum_a(s_a-1)\alpha_a\right]$, in the generating function equation (7.7.52) we can always make the interchangeable choice

$$\partial_a \leftrightarrow \partial_a^x \leftrightarrow -\mathrm{i}\partial_a^y\,. \tag{7.7.58}$$

We then substitute the form (7.7.54) for B_{ab}, and replace ∂_a by either ∂_a^x or $-\mathrm{i}\partial_a^y$

according to whether the corresponding index on $\boldsymbol{A}$ or $\underset{\sim}{C}$ is x or y respectively. We then derive

$$\begin{aligned}\partial_t G(\boldsymbol{s}, t) = \int d^2\boldsymbol{\alpha} f(\boldsymbol{\alpha}, t)\{[\sum_a (A_{a;x}\partial_a^x + A_{a;y}\partial_a^y) \\ + \tfrac{1}{2}\sum_{a,b,c}(C_{a,c,x}C_{c,b;x}\partial_a^x\partial_b^x + C_{a,c;y}C_{c,b;y}\partial_a^y\partial_b^y \\ + 2C_{a,c;x}C_{c,b;y}\partial_a^x\partial_b^y]\exp[\sum_a (s_a - 1)\alpha_a]\}\,.\end{aligned} \tag{7.7.59}$$

Integrating by parts and discarding the surface terms to get a FPE in the variables $(\boldsymbol{\alpha}_x, \boldsymbol{\alpha}_y)$,

$$\begin{aligned}\partial_t f(\boldsymbol{\alpha}, t) = [-\sum_a (\partial_a^x A_{a;x} + \partial_a^y A_{a;y}) + \tfrac{1}{2}\sum_{a,b,c}(\partial_a^x\partial_b^x C_{a,c;x}C_{c,b;x} \\ + \partial_a^y\partial_b^y C_{a,c;y}C_{c,b;y} + 2\partial_a^x\partial_b^y C_{a,c;x}C_{c,b;y})]f(\boldsymbol{\alpha}, t)\,.\end{aligned} \tag{7.7.60}$$

In the space of doubled dimensions, this is a FPE with positive semidefinite diffusion. For, we have for the variable $(\boldsymbol{\alpha}_x, \boldsymbol{\alpha}_y)$ the drift vector

$$\mathscr{A}(\boldsymbol{\alpha}) = [\boldsymbol{A}_x(\boldsymbol{\alpha}), \boldsymbol{A}_y(\boldsymbol{\alpha})] \tag{7.7.61}$$

and the diffusion matrix

$$\mathscr{B}(\boldsymbol{\alpha}) = \begin{bmatrix} \underset{\sim}{C}_x\underset{\sim}{C}_x^{\mathrm{T}} & \underset{\sim}{C}_x\underset{\sim}{C}_y^{\mathrm{T}} \\ \underset{\sim}{C}_y\underset{\sim}{C}_x^{\mathrm{T}} & \underset{\sim}{C}_y\underset{\sim}{C}_y^{\mathrm{T}} \end{bmatrix} = \mathscr{C}(\boldsymbol{\alpha})\mathscr{C}(\boldsymbol{\alpha})^{\mathrm{T}} \tag{7.7.62}$$

where

$$\mathscr{C}(\boldsymbol{\alpha}) = \begin{bmatrix} \underset{\sim}{C}_x & 0 \\ \underset{\sim}{C}_y & 0 \end{bmatrix} \tag{7.7.63}$$

so that $\mathscr{B}(\boldsymbol{\alpha})$ is explicitly positive semidefinite.

b) Stochastic Differential Equation (SDE)

Corresponding to the drift and diffusion (7.7.61, 62) we have a stochastic differential equation

$$\begin{bmatrix} d\boldsymbol{\alpha}_x \\ d\boldsymbol{\alpha}_y \end{bmatrix} = \begin{bmatrix} \boldsymbol{A}_x(\alpha) \\ \boldsymbol{A}_y(\alpha) \end{bmatrix} dt + \begin{bmatrix} \underset{\sim}{C}_x d\boldsymbol{W}(t) \\ \underset{\sim}{C}_y d\boldsymbol{W}(t) \end{bmatrix} \tag{7.7.64}$$

where $\boldsymbol{W}(t)$ is a Wiener process of the same dimension as $\boldsymbol{\alpha}_x$. Note that the same Wiener process occurs in both lines because of the two zero entries $\mathscr{C}(\boldsymbol{\alpha})$ as written in (7.7.63).

Recombining real and imaginary parts, we find the SDE for the complex variable $\boldsymbol{\alpha}$:

$$d\boldsymbol{\alpha} = \boldsymbol{A}(\boldsymbol{\alpha})dt + \underset{\sim}{C}(\boldsymbol{\alpha})d\boldsymbol{W}(t)\,. \tag{7.7.65}$$

This is of course, exactly the same SDE which would arise if we used the usual rules for converting Fokker-Planck equations to stochastic differential equations directly on the Poisson representation FPE (7.7.9), and ignored the fact that $\underset{\sim}{C}(\boldsymbol{\alpha})$ so defined would have complex elements if $\underset{\sim}{\boldsymbol{B}}$ was not a positive semidefinite diffusion matrix.

c) Examples of Stochastic Differential Equations in the Complex Plane

We again consider the reactions (sect. 7.7.b)

$$\begin{aligned} A + X &\underset{k_4}{\overset{k_2}{\rightleftharpoons}} 2X \\ B + X &\underset{k_3}{\overset{k_1}{\rightleftharpoons}} C\,. \end{aligned} \tag{7.7.66}$$

The use of the positive Poisson representation applied to this system yields the SDE, arising from the FPE (7.7.16):

$$d\alpha = [k_3C + (k_2A - k_1B)\alpha - k_4\alpha^2]dt + [2(k_2A\alpha - k_4\alpha^2)]^{1/2}dW(t)\,. \tag{7.7.67}$$

In the case $\delta > 0$, we note that the noise term vanishes at $\alpha = 0$ and at $\alpha = k_2A/k_4$, is positive between these points and the drift term is such as to return α to the range $[0, k_2A/k_4]$ whenever it approaches the end points. Thus, for $\delta > 0$, (7.7.67) represents a real SDE on the real interval $[0, k_2A/k_4]$.

In the case $\delta < 0$, the stationary point lies outside the interval $[0, k_2A/k_4]$, and a point initially in this interval will move along this interval governed by (7.7.67) until it meets the right-hand end, where the noise vanishes and the drift continues to drive it towards the right. One leaving the interval, the noise becomes imaginary and the point will follow a path like that shown in Fig. 7.4 until it eventually reaches the interval $[0, k_2A/k_4]$ again.

The case of $\delta = 0$ is not very dissimilar, except that once the point reaches the right-hand end of the interval $[0, k_2A/k_4]$, both drift and diffusion vanish so it remains there from then on.

In the case of the system

$$\begin{aligned} &B \to X \\ &2X \to A\,, \end{aligned} \tag{7.7.68}$$

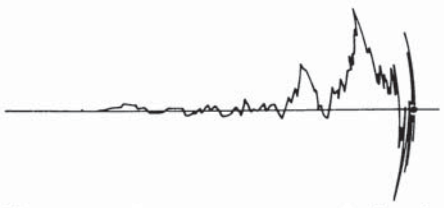

Fig. 7.4. Path followed by a point obeying the stochastic differential equation (7.7.67)

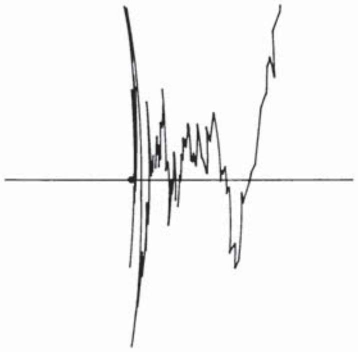

Fig. 7.5. Simulation of the path of a point obeying the stochastic differential equation (7.7.69) ▶

the SDE coming from the FPE (7.7.41) is

$$d\eta/dt = \kappa_1 - 2\kappa_2\eta^2 + i\varepsilon(2\kappa_2)^{1/2}\eta\xi(t)\,, \tag{7.7.69}$$

where $\alpha = \eta V$ and $\varepsilon = V^{-1/2}$.

The SDE (7.7.69) can be computer simulated and a plot of motion in the complex η plane generated. Figure 7.5 illustrates the behaviour. The point is seen to remain in the vicinity of $\mathrm{Re}\{\alpha\} = (a/2)^{1/2}$ but to fluctuate mainly in the imaginary direction on either side, thus giving rise to a negative variance in α.

7.7.5 Time Correlation Functions

The time correlation function of a Poisson variable $\boldsymbol{\alpha}$ is not the same as that for the variable $\boldsymbol{x}$. This can be seen, for example, in the case of a reaction $X \leftrightarrows Y$ which gives a Poisson Representation Fokker-Planck equation with no diffusion term. Hence, the Poisson variable does not fluctuate. We now show what the relationship is. For clarity, the demonstration is carried out for one variable only.

We define

$$\langle\alpha(t)\alpha(s)\rangle = \int d\mu(\alpha)d\mu(\alpha')\alpha\alpha' f(\alpha, t\,|\,\alpha', s)f(\alpha', s)\,. \tag{7.7.70}$$

We note that

$$f(\alpha, s\,|\,\alpha', s) = \delta_\mu(\alpha - \alpha')$$

which means that

$$\int d\mu(\alpha)\, e^{-\alpha}(\alpha^x/x!)f(\alpha, s\,|\,\alpha', s) = e^{-\alpha'}\alpha'^x/x! \tag{7.7.71}$$

so that

$$\int d\mu(\alpha)\,\alpha f(\alpha, t\,|\,\alpha', s) = \sum_{x,x'} xP(x, t\,|\,x', s)e^{-\alpha'}\alpha'^{x'}/x'!$$

Hence,

$$\begin{aligned}\langle\alpha(t)\alpha(s)\rangle &= \sum_{x,x'} xP(x, t\,|\,x', s)\int d\mu(\alpha')(\alpha'^{x'+1}e^{-\alpha'}/x'!)f(\alpha', s)\\ &= \sum_{x,x'} xP(x, t\,|\,x', s)\int d\mu(\alpha')\left[\left(-\alpha'\frac{\partial}{\partial\alpha'} + x'\right)(\alpha'^{x'}e^{-\alpha'}/x'!)\right]f(\alpha', s)\\ &= \sum_{x,x'} x\,x'P(x, t\,|\,x', s)P(x', s) \qquad (7.7.72)\\ &\quad - \int d\mu(\alpha')f(\alpha', s)\alpha'\frac{\partial}{\partial\alpha'}\sum_{x,x'} xP(x, t\,|\,x', s)(\alpha'^{x'}e^{-\alpha'}x!)\,. \qquad (7.7.73)\end{aligned}$$

We define

$$\langle\alpha(t)\,|\,[\alpha', s]\rangle \equiv \int d\alpha\,\alpha f(\alpha, t\,|\,\alpha', s) \tag{7.7.74}$$

as the mean of $\alpha(t)$ given the initial condition α' at s. Then the second term can be written

$$-\int d\mu(\alpha')\alpha'\frac{\partial}{\partial\alpha'}\langle\alpha(t)\,|\,[\alpha', s]\rangle f(\alpha', s) \equiv \left\langle\alpha'\frac{\partial}{\partial\alpha'}\langle\alpha(t)\,|\,[\alpha, s]\rangle\right\rangle \tag{7.7.75}$$

so we have

$$\langle x(t)x(s)\rangle = \langle\alpha(t)\alpha(s)\rangle + \left\langle\alpha'\frac{\partial}{\partial\alpha'}\langle\alpha(t)\,|\,[\alpha, s]\rangle\right\rangle\,. \tag{7.7.76}$$

Taking into account a many-variable situation and noting that

$$\langle\boldsymbol{x}(t)\rangle = \langle\boldsymbol{\alpha}(t)\rangle \qquad \text{always}\,,$$

we have

$$\boxed{\langle x_a(t), x_b(s)\rangle = \langle\alpha_a(t), \alpha_b(s)\rangle + \left\langle\alpha_b'\frac{\partial}{\partial\alpha_b'}\langle\alpha_a(t)\,|\,[\boldsymbol{\alpha}', s]\rangle\right\rangle\,.} \tag{7.7.77}$$

This formula explicitly shows the fact that the Poisson representation gives a process which is closely related to the Birth-Death Master equation, but not isomorphic to it. The stochastic quantities of interest, such as time correlation functions, can all be calculated but are not given directly by those of the Poisson variable.

a) Interpretation in Terms of Statistical Mechanics

We assume for the moment that the reader is acquainted with the statistical mechanics of chemical systems. If we consider a system composed of chemically reacting components $A, B, C, \ldots$, the distribution function in the grand canonical ensemble is given by

$$P(I) = \exp\{\beta[\Omega + \sum_i \mu_i x_i(I) - E(I)]\}\,, \tag{7.7.78}$$

where I is an index describing the microscopic state of the system, $x_i(I)$ is the number of molecules of X_i in the state I, $E(I)$ is the energy of the state, μ_i is the chemical potential of component X_i, Ω is a normalization factor, and

$$\beta = 1/kT\,. \tag{7.7.79}$$

The fact that the components can react requires certain relationships between the chemical potentials to be satisfied, since a state I can be transformed into a state J only if

$$\sum_i \nu_i^A x_i(I) = \sum_i \nu_i^A x_i(J)\,, \qquad A = 1, 2, 3, \ldots \tag{7.7.80}$$

where ν_a^A are certain integers. The relations (7.7.80) are the stoichiometric constraints.

The canonical ensemble for a reacting system is defined by requiring

$$\sum_i \nu_i^A x_i(I) = \tau^A\,, \tag{7.7.81}$$

for some τ^A, whereas the grand canonical ensemble is defined by requiring

$$\sum_I P(I) \sum_i \nu_i^A x_i(I) \equiv \sum_i \nu_i^A \langle x_i \rangle = \tau^A\,, \tag{7.7.82}$$

Maximization of entropy subject to the constraint (7.7.82) (and the usual constraints of fixed total probability and mean energy) gives the grand canonical form (7.7.78) in which the chemical potentials also satisfy the relation

$$\mu_i = \sum_A k_A \nu_i^A\,. \tag{7.7.83}$$

When one takes the ideal solution or ideal gas limit, in which interaction energies (but not kinetic or internal energies) are neglected, there is no difference between the distribution function for an ideal reacting system and an ideal nonreacting system, apart from the requirement that the chemical potentials be expressible in the form of (7.7.83).

The canonical ensemble is not so simple, since the constraints must appear explicitly as a factor of the form

$$\prod_A \delta[\sum_i \nu_i^A x_i(I), \tau^A] \tag{7.7.84}$$

and the distribution function is qualitatively different for every kind of reacting system (including a nonreacting system as a special case).

The distribution in total numbers $\boldsymbol{x}$ of molecules of reacting components in the grand canonical ensemble of an ideal reacting system is easily evaluated, namely,

$$P(\boldsymbol{x}) = \exp[\beta(\Omega + \sum_i \mu_i x_i)] \sum_I \prod_i \delta[x_i(I), x_i] \exp[-\beta E(I)]\,. \tag{7.7.85}$$

The sum over states is the same as that for the canonical ensemble of an ideal nonreacting mixture so that

$$P(\boldsymbol{x}) = \exp[\beta(\Omega + \sum_i \mu_i x_i)] \prod_i \frac{1}{x_i!} \{\sum_k \exp[-\beta E_k(i)]\}^{x_i}\,, \tag{7.7.86}$$

where $E_k(i)$ are the energy eigenstates of a single molecule of the substance A. This result is a multivariate Poisson with mean numbers given by

$$\log\langle x_i \rangle = \beta\mu_i - \log[\sum_k e^{-\beta E_k(i)}] \tag{7.7.87}$$

which, as is well known, when combined with the requirement (7.7.82) gives the law of mass action.

The canonical ensemble is obtained by maximizing entropy subject to the stronger constraint (7.7.81), which implies the weak constraint (7.7.82). Thus, the distribution function in total numbers for the canonical ensemble will simply be given by

$$P(\boldsymbol{x}) \propto \left\{\prod_i \frac{1}{x_i!} [\sum_k e^{-\beta E_k(i)}]^{x_i}\right\} \sum_A \delta[\sum_i \nu_i^A x_i, \tau^A]\,. \tag{7.7.88}$$

In terms of the Poisson representation, we have just shown that in equilibrium situations, the quasiprobability (in a grand canonical ensemble) is

$$f(\boldsymbol{\alpha})_{eq} = \delta[\boldsymbol{\alpha} - \boldsymbol{\alpha}(eq)] \tag{7.7.89}$$

since the $\boldsymbol{x}$ space distribution is Poissonian. For the time correlation functions there are two results of this.

i) The variables $\boldsymbol{\alpha}(t)$ and $\boldsymbol{\alpha}(s)$ are nonfluctuating quantities with values $\boldsymbol{\alpha}(eq)$. Thus,

$$\langle \alpha_r(t), \alpha_s(s) \rangle_{eq} = 0\,. \tag{7.7.90}$$

ii) The equilibrium mean in the second term is trivial. Thus,

$$\langle x_a(t), x_b(s) \rangle = \left[\alpha_b' \frac{\partial}{\partial \alpha_b'} \langle \alpha_a(t) | [\boldsymbol{\alpha}', s] \rangle\right]_{\boldsymbol{\alpha}' = \boldsymbol{\alpha}(eq)}\,. \tag{7.7.91}$$

This result is, in fact, exactly that of *Bernard* and *Callen* [7.11] which relates a two-time correlation function to a derivative of the mean of a quantity with respect to a thermodynamically conjugate variable.

Consider a system in which the numbers of molecules of chemical species X_1, X_2, ... corresponding to a configuration I of the system are $x_1(I)$, $x_2(I)$. ... and it is understood that these chemical species may react with each other. Then in a grand canonical ensemble, as demonstrated above, the equilibrium distribution function is

$$Z^{-1}(\boldsymbol{\mu}) \exp[\{\sum_i \mu_i x_i(I) - E(I)\}/kT] \tag{7.7.92}$$

with

$$Z(\boldsymbol{\mu}) = \exp(-\Omega\beta)\,, \tag{7.7.93}$$

where $Z(\boldsymbol{\mu})$ is the grand canonical partition function. As pointed out above, the chemical potentials μ_i for a reacting system cannot be chosen arbitrarily but must be related by the stoichiometric constraints (7.7.82) of the allowable reactions.

Now we further define the quantities

$$\langle x_i, t | [I, s] \rangle \tag{7.7.94}$$

to be the mean values of the quantities x_i at time t under the condition that the system was in a configuration I at time s. Then a quantity of interest is the mean value of (7.7.94) over the distribution (7.7.92) of initial conditions, namely,

$$\langle x_i, t\,|\,[\boldsymbol{\mu}, s]\rangle = \sum_J \langle x_i, t\,|\,[J, s]\rangle Z^{-1}(\boldsymbol{\mu})$$
$$\times \exp\left\{\frac{1}{kT}\left[\sum_j \mu_j x_j(J) - E(J)\right]\right\}. \tag{7.7.95}$$

When the chemical potentials satisfy the equilibrium constraints, this quantity will be time independent and equal to the mean of x_i in equilibrium, but otherwise it will have a time dependence. Then, with a little manipulation one finds that

$$\left[kT\frac{\partial}{\partial\mu_j}\langle x_i, t\,|\,[\boldsymbol{\mu}, s]\rangle\right]_{\mu=\mu(eq)} = \langle x_i(t), x_j(s)\rangle_{eq}\,. \tag{7.7.96}$$

The left-hand side is a reponse function of the mean value to the change in the chemical potentials around equilibrium and is thus a measure of dissipation, while the right-hand side, the two-time correlation function in equilibrum, is a measure of fluctuations.

To make contact with the Poisson representation result (7.7.91) we note that the chemical potentials μ_j in ideal solution theory are given by

$$\mu_i(\langle \boldsymbol{x}\rangle) = kT\log\langle x_i\rangle + \text{const}\,. \tag{7.7.97}$$

Using (7.7.97), we find that (7.7.96) becomes

$$\langle x_i(t), x_j(s)\rangle = \left[\langle x_j\rangle\frac{\partial}{\partial\langle x_j\rangle}\langle x_i, t\,|\,[\boldsymbol{\mu}(\langle\boldsymbol{x}\rangle), s]\rangle\right]_{\langle\boldsymbol{x}\rangle=\langle\boldsymbol{x}\rangle_{eq}}. \tag{7.7.98}$$

Since the ideal solution theory gives rise to a distribution in x_i that is Poissonian, it follows that in that limit

$$\langle x_i, t\,|\,[\boldsymbol{\mu}(\langle\boldsymbol{x}\rangle), s]\rangle = \langle \alpha_i, t\,|\,[\boldsymbol{\alpha}', s]\rangle \tag{7.7.99}$$

with $\alpha' = \langle\boldsymbol{x}\rangle$. Thus, (7.7.98) becomes

$$\langle x_i(t), x_j(s)\rangle = \left[\alpha'_j\frac{\partial}{\partial\alpha_j}\langle\alpha_i, t\,|\,[\boldsymbol{\alpha}', s]\rangle\right]_{\alpha'=\alpha(eq)}. \tag{7.7.100}$$

Thus, (7.7.91) is the ideal solution limit of the general result (7.7.98).

The general formula (7.7.77) can be considered as a generalization of the Bernard-Callen result to systems that are not in thermodynamic equilibrium.

However, it is considerably different from the equilibrium result and the two terms are directly interpretable. The second term is the equilibrium contribution, a response function, but since the system is not in a well-defined equilibrium state, we take the average of the equilibrium result over the various contributing α space states. The first term is the contribution from the α-space fluctuations themselves and is not directly related to a response function. It represents the fluctuations in excess of equilibrium.

b) Linearised Results

The general differential equation, arising from the use of the positive Poisson representation, and corresponding to the FPE (7.7.12), is

$$d\boldsymbol{\eta} = \hat{\boldsymbol{A}}(\boldsymbol{\eta})dt + \varepsilon\hat{\underset{\sim}{C}}(\boldsymbol{\eta})d\boldsymbol{W}(t)\,, \tag{7.7.101}$$

where

$$\hat{\underset{\sim}{C}}\hat{\underset{\sim}{C}}^{\mathrm{T}} = \hat{\underset{\sim}{B}}\,. \tag{7.7.102}$$

We may now make a first-order small noise expansion about the stationary state $\boldsymbol{\eta}$ by following the procedure of Sect.6.3. Thus, writing

$$\boldsymbol{\eta}(t) = \bar{\boldsymbol{\eta}} + \varepsilon\boldsymbol{\eta}_1(t) \qquad (\varepsilon = V^{-1/2}) \tag{7.7.103}$$

to lowest order we have

$$\hat{\boldsymbol{A}}(\bar{\boldsymbol{\eta}}) = 0 \tag{7.7.104}$$
$$d\boldsymbol{\eta}_1 = -\boldsymbol{F}\boldsymbol{\eta}_1 dt + \underset{\sim}{G}\,d\boldsymbol{W}(t)$$

where

$$F_{rs} = -\frac{\partial}{\partial\eta_s}\hat{A}_r(\bar{\boldsymbol{\eta}}) \tag{7.7.105}$$
$$\underset{\sim}{G} = \hat{\underset{\sim}{C}}(\bar{\boldsymbol{\eta}})\,.$$

Then,

$$\langle\alpha_r(t), \alpha_s(0)\rangle_s = V\sum_{r'}[\exp(-\boldsymbol{F}t)]_{rr'}\langle\eta_{r',1}, \eta_{s,1}\rangle_s \tag{7.7.106}$$

and

$$\frac{\partial}{\partial\alpha'_s}\langle\alpha_r(t)\,|\,[\boldsymbol{\alpha}', 0]\rangle = \frac{\partial}{\partial\eta'_{s,1}}\langle\eta_{r,1}(t)\,|\,[\boldsymbol{\eta}'_1, 0]\rangle = [\exp(-Ft)]_{r,s}\,. \tag{7.7.107}$$

Hence,

$$\langle x_r(t), x_s(0)\rangle_s = V\sum_{r'}[\exp(-Ft)]_{rr'}[\langle\eta_{r',1}, \eta_{s,1}\rangle_s + \delta_{r',s}\bar{\eta}_s) \tag{7.7.108}$$
$$= \sum_{r'}\exp(-Ft)_{r,r'}\langle x_r, x_s\rangle_s\,. \tag{7.7.109}$$

Thus the linearised result is in agreement with the regression theorem of sect. 3.7.4 correlation functions for a variety of systems nave been computed in [7.10].

7.7.6 Trimolecular Reaction

In Sect. 7.1.3 we considered a reaction which included a part

$$A + 2X \rightleftharpoons 3X \tag{7.7.110}$$

and set up an appropriate birth-death Master equation for this. However, it is well known in chemistry that such trimolecular steps are of vanishingly small probability and proceed in stages via a short-lived intermediate. Thus, the reaction (7.7.110) presumably occurs as a two-state system

$$\text{i)}\quad A + Y \underset{1}{\overset{1}{\rightleftharpoons}} X + Y \tag{7.7.111a}$$

$$\text{ii)}\quad Y \underset{1}{\overset{\gamma}{\rightleftharpoons}} 2X\,, \tag{7.7.111b}$$

both of which are merely bimolecular, and we have set rate constants equal to one, except for γ (the decay constant of Y) which is assumed as being very large. Thus, Y is indeed a short-lived intermediate. The deterministic rate equations are

$$\begin{aligned} \frac{dx}{dt} &= ay - xy + 2(\gamma y - x^2) \\ \frac{dy}{dt} &= x^2 - \gamma y \end{aligned} \tag{7.7.112}$$

and the usual deterministic adiabatic elimination procedure sets $y = x^2/\gamma$ and gives

$$\frac{dx}{dt} = (ax^2 - x^3)/\gamma\,. \tag{7.7.113}$$

Although this procedure is straightfoward deterministically, it is not clear that the stochastic Master equation of the kind used in Sect.7.1.3 is a valid adiabatic elimination limit. The adiabatic elimination techniques used in Chap. 6 are not easily adapted to direct use on a Master equation but can be straightfowardly adapted to the case of the Poisson representation Fokker-Planck equation.

a) Fokker-Planck Equation for Trimolecular Reaction
For the reaction (7.7.110) with forward and backward rate constants equal to $1/\gamma$ to correspond to (7.7.113), the Poisson representation Fokker-Planck equation becomes, from (7.7.4),

$$\frac{\partial f}{\partial t} = \frac{1}{\gamma}\left\{\left(-\frac{\partial}{\partial\alpha} + 2\frac{\partial^2}{\partial\alpha^2} - \frac{\partial^3}{\partial\alpha^3}\right)[\alpha^2(a-\alpha)]f\right\} \tag{7.7.114}$$

and contains *third-order derivatives.* There is no truly probabilistic interpretation in terms of any real stochastic process in α space, no matter what kind of Poisson representation is chosen. The concept of *third-order noise* will be explained in the next section, which will show how probabilistic methods and stochastic differential equations can still be used.

b) Adiabatic Elimination
Using the rules developed in (7.4.9), the Fokker-Planck equation for the system (7.7.111) with the correspondence

$$\begin{bmatrix} x \\ y \end{bmatrix} \leftrightarrow \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

is

$$\begin{aligned} \frac{\partial f}{\partial\alpha} = &-\frac{\partial}{\partial\alpha}[(a-\alpha)\beta + 2(\gamma\beta - \alpha^2)] + \frac{\partial}{\partial\beta}(\gamma\beta - \alpha^2) \\ &+ \frac{\partial^2}{\partial\alpha^2}(\gamma\beta - \alpha^2) + \frac{\partial^2}{\partial\alpha\partial\beta}[(a-\alpha)\beta]\,. \end{aligned} \tag{7.7.115}$$

Adiabatic elimination now proceeds as in Sect.6.6.1. We define new variables

$$\begin{aligned} x &= \alpha \\ y &= \gamma\beta - \alpha^2 \end{aligned} \tag{7.7.116}$$

and consequently, changing variables with

$$\begin{aligned} \frac{\partial}{\partial\alpha} &= \frac{\partial}{\partial x} - 2x\frac{\partial}{\partial y} \\ \frac{\partial}{\partial\beta} &= \gamma\frac{\partial}{\partial y}, \end{aligned} \tag{7.7.117}$$

the FPE becomes

$$\begin{aligned} \frac{\partial f(x,y)}{\partial t} = &\left\{-\left(\frac{\partial}{\partial x} - 2x\frac{\partial}{\partial y}\right)\left[\frac{(a-x)(y+x^2)}{\gamma} + 2y\right] + \gamma\frac{\partial}{\partial y}y\right. \\ &\left.+\left(\frac{\partial}{\partial x} - 2x\frac{\partial}{\partial y}\right)\left(\frac{\partial}{\partial x} - 2x\frac{\partial}{\partial y}\right)y + \left(\frac{\partial}{\partial x} - 2x\frac{\partial}{\partial y}\right)\left(\frac{\partial}{\partial y}\right)[(y+x^2)(a-x)]\right\}f. \end{aligned} \tag{7.7.118}$$

Since y is to be eliminated, there should be a well-defined limit of the L_1 operator which governs its motion at fixed x. However, this operator is

$$\gamma\frac{\partial}{\partial y}y + \frac{\partial^2}{\partial y^2}[4x^2y - 2x(y+x^2)(a-x)] \tag{7.7.119}$$

and the large γ limit turns this into deterministic motion. Setting

$$y = v\gamma^{-1/2} \tag{7.7.120}$$

transforms(7.7.119) to

$$\begin{aligned} \gamma L_1(\gamma) &= \gamma\left\{\frac{\partial}{\partial v}v + \frac{\partial^2}{\partial v^2}[2x^3(x-a) + (4x^2 - 2x)v\gamma^{-1/2}]\right\} \\ &\xrightarrow[\gamma\to\infty]{} \gamma\left\{\frac{\partial}{\partial v}v + \frac{\partial^2}{\partial v^2}[2x^3(x-a)]\right\} \\ &\equiv \gamma L_1\,. \end{aligned} \tag{7.7.121}$$

With this substitution, we finally identify

$$\gamma^{-1}L_3 = -\gamma^{-1}\frac{\partial}{\partial x}[x^2(a-x)] \tag{7.7.122}$$

$$L_2(\gamma) = -\frac{\partial}{\partial x}[(a-x)v\gamma^{-3/2} + 2v\gamma^{-1/2}] - \frac{\partial}{\partial x}2x\frac{\partial}{\partial v}v - 2x\frac{\partial}{\partial v}\frac{\partial}{\partial x}v$$
$$+ \gamma^{-1/2}\frac{\partial^2}{\partial x^2}v + \gamma^{1/2}\frac{\partial}{\partial x}\frac{\partial}{\partial v}[(a-x)(x^2+v\gamma^{-1/2})] \tag{7.7.123}$$

and

$$\frac{\partial f}{\partial t} = [\gamma^{-1}L_3 + L_2(\gamma) + \gamma L_1(\gamma)]f. \tag{7.7.124}$$

The projection operator P will be onto the null space of L_1 and because L_1 depends on x, we have

$$L_3 P \neq PL_3. \tag{7.7.125}$$

This means that the equation of motion for $Pf \equiv g$ is found by similar algebra to that used in Sect. 6.5.4. We find

$$s\tilde{g}(s) = \gamma^{-1}PL_3\tilde{g}(s) + P[L_2(\gamma) + \gamma^{-1}L_3][s - \gamma L_1 - (1-P)L_2(\gamma) - \gamma^{-1}(1-P)L_3]^{-1}$$
$$\times [L_2(\gamma) + \gamma^{-1}(1-P)L_3]\tilde{g}(s) + g(0). \tag{7.7.126}$$

Notice, however, since for any function of v

$$P\phi(v) = p_x(v)\int dv\,\phi(v) \tag{7.7.127}$$

where $p_x(v)$ satisfies

$$L_1 p_x(v) = 0, \tag{7.7.128}$$

that in $PL_2(\gamma)$, all terms with $\partial/\partial v$ in them vanish. Thus, to highest order in γ,

$$PL_2(\gamma) = \gamma^{-1/2}\left(-2v\frac{\partial}{\partial x} + v\frac{\partial^2}{\partial x^2}\right). \tag{7.7.129}$$

The term $[\ ]^{-1}$ in (7.7.126) is asymptotic to $-\gamma^{-1}L_1^{-1}$ and the only term in the remaining bracket which can make the whole expression of order γ^{-1}, like the L_3 term, is the term of order $\gamma^{1/2}$ in $L_2(\gamma)$, i.e.,

$$\gamma^{1/2}\frac{\partial}{\partial x}[(a-x)x^2]\frac{\partial}{\partial v}. \tag{7.7.130}$$

Thus, the large γ limit of (7.7.126) is

$$s\tilde{g}(s) = \gamma^{-1}\left\{PL_3\tilde{g} - P\left[-2\frac{\partial}{\partial x} + \frac{\partial^2}{\partial x^2}\right]vL_1^{-1}\frac{\partial}{\partial x}\left[(a-x)x^2\frac{\partial}{\partial v}\right]p_x(v)\tilde{p}\right\} + g(0) \tag{7.7.131}$$

where we have written

$$g = p_x(v)p, \qquad \tilde{g} = p_x(v)\tilde{p}. \tag{7.7.132}$$

We are now lead to the central problem of the evaluation of

$$\int dv'v'L_1^{-1}\frac{\partial}{\partial x}(a-x)x^2\frac{\partial}{\partial v'}p_x(v') \tag{7.7.133}$$

which arises in the evaluation of the second part in the braces in (7.7.131). We wish to bring the $\partial/\partial x$ to the left outside the integral, but since $\partial/\partial x$ and L_1 do not commute, this requires care. Now

$$\left[L_1^{-1}, \frac{\partial}{\partial x}\right] = L_1^{-1}\left[\frac{\partial}{\partial x}, L_1\right]L_1^{-1} \tag{7.7.134}$$

and from (7.7.121),

$$= L_1^{-1}\left\{\frac{\partial^2}{\partial v^2}[8x^3 - 6ax^2]\right\}L_1^{-1}; \tag{7.7.135}$$

$$(7.7.133) = \frac{\partial}{\partial x}\int dv'v'L_1^{-1}(a-x)x^2\frac{\partial}{\partial v'}p_x(v')$$
$$+ \int dv'v'L_1^{-1}\frac{\partial^2}{\partial v'^2}L_1^{-1}[(8x^3 - 6ax^2)(a-x)x^2]\frac{\partial}{\partial v'}p_x(v'). \tag{7.7.136}$$

The second term vanishes, through the demonstration that this is so is rather specialised. For, we know that L_1 describes an Ornstein-Uhlenbeck process in v and that $p_x(v)$ is its stationary solution. The eigenfunction properties used in Sect.6.4.2 show that

$$L_1^{-1}\frac{\partial^2}{\partial v^2}L_1^{-1}\frac{\partial}{\partial v}p_x(v) \tag{7.7.137}$$

is proportional to the third eigenfunction, which is orthogonal to v, the first eigenfunction of the corresponding backward equation. The first term is now easily computed using the fact that L_1 involves the Ornstein-Uhlenbeck process. Using the same techniques as in Sect.6.6.1, we find that all the x dependence arising from $p_x(v')$ vanishes, and hence

$$(7.7.133) = \frac{\partial}{\partial x}(a-x)x^2. \tag{7.7.138}$$

We similarly find

$$PL_3\tilde{g} = -p_x(v) \int dv' \frac{\partial}{\partial x}[x^2(a-x)]p_x(v')\tilde{p}$$

$$= -p_x(v)\frac{\partial}{\partial x}[x^2(a-x)]\tilde{p}\,, \tag{7.7.139}$$

so in the end

$$\frac{\partial p}{\partial t} = \frac{1}{\gamma}\left[\left(-\frac{\partial}{\partial x} + 2\frac{\partial^2}{\partial x^2} - \frac{\partial^3}{\partial x^3}\right)[(a-x)x^2]p\right] \tag{7.7.140}$$

which is exactly the same as the trimolecular model Fokker-Planck equation (7.7.114). This means the trimolecular Master equation is valid in the same limit.

c) Comments

i) Notice that this system gives an end result which is *not* in a Stratonovich form but in the Ito form, with all derivatives to the left.

ii) The derivation of (7.7.140) means that techniques for understanding such non-probabilistic Fokker-Planck equations are required. We outline a possible way of doing this in the next section.

7.7.7 Third-Order Noise

To handle the third-order Fokker-Planck equations which arise with trimolecular reactions, we introduce the stochastic variable $V(t)$ whose conditional probability density $p(v, t)$ obeys the third-order partial differential equation

$$\partial p(v,t)/\partial t = -\tfrac{1}{6}\,\partial^3 p(v,t)/\partial v^3\,. \tag{7.7.141}$$

Since we have already shown in Sect.3.4 that no Markov process can possible give a third-order term like this, some fundamental requirement must be violated by $p(v, t)$. It turns out that $p(v, t)$ is not always positive, which is permissible in a quasi-probability. We will see that in spite of this, the formal probabilistic analogy is very useful.

We know that the solution of (7.7.141), subject to the boundary condition

$$p(v, t_0) = \delta(v - v_0)\,, \tag{7.7.142}$$

is given by Fourier transform methods as

$$p(v, t\,|\,v_0, t_0) = (1/2\pi)\int_{-\infty}^{\infty} dq \exp\{i[q(v-v_0) + \tfrac{1}{6}q^3(t-t_0)]\}\,. \tag{7.7.143}$$

The moments of V can be calculated, after a partial integration, to be

$$\begin{aligned} &\langle[V(t) - V_0]^n\rangle = 0, \qquad\qquad n \text{ not a multiple of } 3 \\ &\langle[V(t) - V_0]^{3m}\rangle = [(t-t_0)/6]^m(3m)!/m!\,. \end{aligned} \tag{7.7.144}$$

Further, we assume the process (7.7.141) is some kind of generalized Markov process, for which the joint probability distribution is given by

$$p(v_2t_2 : v_1t_1) = p(v_2t_2\,|\,v_1t_1)p(v_1, t_1) \tag{7.7.145}$$

and from (7.7.142) we see that the first factor is a function of only $v_2 - v_1$ and $t_2 - t_1$, so that the variable $V(t_2) - V(t_1)$ is statistically independent of $V(t_1)$ and that this process is a *process with independent increments*. Thus, $dV(t)$ will be independent of $V(t)$.

The rigorous definition of stochastic integration with respect to $V(t)$ is a task that we shall not attempt at this stage. However, it is clear that it will not be too dissimilar to Ito integration and, in fact, *Hochberg* [7.12] has rigorously defined higher-order noises of even degree and carried out stochastic integration with respect to them. We can show, however, that a stochastic differential equation of the form

$$dy(t) = a(y)dt + b(y)dW(t) + c(y)dV(t) \tag{7.7.146}$$

[with $W(t)$ and $V(t)$ independent processes] is equivalent to a third-order Fokker-Planck equation. It is clear that because $W(t)$ and $V(t)$ are processes with independent increments, $y(t)$ is a Markov process. We then calculate

$$\lim_{t\to t_0}\frac{\langle[y(t) - y(t_0)]^n\rangle}{t - t_0} = \lim_{dt_0\to 0}\frac{\langle[dy(t_0)]^n\rangle}{dt_0}\,, \tag{7.7.147}$$

where $y(t_0)$ is a numerical initial value, not a stochastic variable. From (7.7.146), $y(t)$ depends on $W(t')$ and $V(t')$ for only $t' \leqslant t$ and, since $dW(t)$ and $dV(t)$ are independent of $y(t)$, we find

$$\begin{aligned} \langle dy(t_0)\rangle &= \langle a[y(t_0)]\rangle dt_0 + \langle b[y(t_0)]\rangle\langle dW(t_0)\rangle + \langle c[y(t_0)]\rangle\langle dV(t_0)\rangle \\ &= \langle a[y(t_0)]\rangle dt_0 = a[y(t_0)]dt_0 \end{aligned} \tag{7.7.148}$$

because $y(t_0)$ is a numerical initial value. Similarly, to lowest order in dt_0

$$\begin{aligned} \langle dy(t_0)^2\rangle &= b[y(t_0)]^2\langle dW(t_0)^2\rangle \\ &= b[y(t_0)]^2 dt_0 \end{aligned} \tag{7.7.149}$$

$$\begin{aligned} \langle dy(t_0)^3\rangle &= c[y(t_0)]^3\langle dV(t_0)^3\rangle \\ &= c[y(t_0)]^3 dt_0\,. \end{aligned} \tag{7.7.150}$$

Thus, we find

$$\left.\begin{aligned} &\lim_{t\to t_0}[\langle y(t) - y(t_0)\rangle/(t-t_0)] = a[y(t_0)] \\ &\lim_{t\to t_0}[\langle[y(t) - y(t_0)]^2\rangle/(t-t_0)] = b[y(t_0)]^2 \\ &\lim\,[\langle]y(t) - y(t_0)]^3\rangle/(t-t_0)] = c[y(t_0)]^3 \end{aligned}\right\} \tag{7.7.151}$$

and all higher powers give a zero result. By utilising a similar analysis to that of Sect. 3.4, this is sufficient to show that $y(t)$ is a generalized diffusion process whose generalized FPE is

$$\frac{\partial p(y,t)}{\partial t} = -\frac{\partial}{\partial y}[a(y)p] + \frac{1}{2}\frac{\partial^2}{\partial y^2}[b(y)^2 p] - \frac{1}{6}\frac{\partial^3}{\partial y^3}[c(y)^3 p]. \tag{7.7.152}$$

We define a noise source $\zeta(t)$ by

$$dV(t) = \zeta(t)dt\,, \tag{7.7.153}$$

where

$$\langle\zeta(t)\rangle = \langle\zeta(t)\zeta(t')\rangle = 0 \tag{7.7.154}$$

$$\langle\zeta(t)\zeta(t')\zeta(t'')\rangle = \delta(t-t')\delta(t'-t'') \tag{7.7.155}$$

and higher moments can be readily calculated from the moments of $dV(t)$. The independence of increments means that, as with the Ito integral, integrals that have a delta-function singularity at their upper limit are to be taken as zero.

Example of the Use of Third-Order Noise. Consider the chemical process

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X \tag{7.7.156}$$

$$A \underset{k_4}{\overset{k_3}{\rightleftharpoons}} X$$

whose Poisson representation FPE is

$$\begin{aligned}\frac{\partial f(\alpha,t)}{\partial t} = &-\frac{\partial}{\partial\alpha}[\kappa_1 V^{-1}\alpha^2 - \kappa_2 V^{-2}\alpha^3 + \kappa_3 V - \kappa_4\alpha)f(\alpha,t)]\\ &+\frac{1}{2}\frac{\partial^2}{\partial\alpha^2}[4(\kappa_1 V^{-1}\alpha^2 - \kappa_2 V^{-2}\alpha^3)f(\alpha,t)]\\ &-\frac{1}{3!}\frac{\partial^3}{\partial\alpha^3}[6(\kappa_1 V^{-1}\alpha^2 - \kappa_2 V^{-2}\alpha^3)f(\alpha,t)]\,,\end{aligned} \tag{7.7.157}$$

where $\kappa_1 V^{-1} = k_1 A$, $\kappa_2 V^{-2} = k_2$, $\kappa_3 V = k_3$, $\kappa_4 = k_4$.

In the steady state, (7.7.157) reduces to a linear second-order differential equation which may be solved in terms of hypergeometric functions, and an asymptotic expansion for the various moments can be obtained using steepest descent methods. This procedure, although possible in principle, is not very practicable. It is in such cases that the method of stochastic differential equations proves to be very useful because of its ease of application.

The stochastic differential equation equivalent to (7.7.157) is

$$\begin{aligned}d\eta(t)/dt = &\,\kappa_1\eta(t)^2 - \kappa_2\eta(t)^3 + \kappa_3 - \kappa_4\eta(t)\\ &+\mu^3\{4[\kappa_1\eta(t)^2 - \kappa_2\eta(t)^3]\}^{1/2}\xi(t)\\ &+\mu^4\{6[\kappa_1\eta(t)^2 - \kappa_2\eta(t)^3]\}^{1/3}\zeta(t)\,,\end{aligned} \tag{7.7.158}$$

where $\alpha = \eta V$, $\mu = V^{-1/6}$ and the noise source $\zeta(t)$, henceforth referred to as the "third-order noise", has been defined in (7.7.153–155)

Equation (7.7.158) may be solved iteratively by expanding $\eta(t)$:

$$\eta(t) = \eta_0(t) + \mu^3\eta_3(t) + \mu^4\eta_4(t) + \mu^6\eta_6(t) + \mu^8\eta_8(t) + \mu^9\eta_9(t) + \dots \tag{7.7.159}$$

which, when substituted in (7.7.158), yields the deterministic equation in the lowest order and linear stochastic differential equations in the higher orders which may be solved as in Sect. 6.2.

In the stationary state the results are

$$\langle x\rangle = V\eta_0 + \langle\eta_6\rangle + \cdots = V\eta_0 + \frac{2ab}{c^2} + \dots \tag{7.7.160a}$$

$$\begin{aligned}\langle x^2\rangle - \langle x^2\rangle &= V\langle\eta_3^2\rangle + [2\langle\eta_9\eta_3\rangle + 2\langle\eta_8\eta_4\rangle + \langle\eta_6^2\rangle - \langle\eta_6\rangle^2 + \langle\eta_6\rangle] + \dots\\ &= V\left[\frac{2a}{c}\right] + \left[\frac{28}{3}\frac{a^2b^2}{c^4} + \frac{8ab^2\eta_0}{c^3} - \frac{36\kappa_2a^2}{c^3} + \frac{8ab}{c^2}\right] + \dots\end{aligned} \tag{7.7.160b}$$

$$\begin{aligned}\langle(x-\langle x\rangle)^3\rangle &= V[\langle\eta_4^3\rangle - 3\langle\eta_3^2\rangle\langle\eta_6\rangle + 3\langle\eta_3^2\rangle + \langle\eta_0\rangle + \dots\\ &= V\left[\frac{8a}{c} - \frac{12a^2b}{c^3} + \eta_0\right] + \dots\,,\end{aligned} \tag{7.7.160c}$$

where $a = \kappa_1\eta_0^2 - \kappa_2\eta_0^3$, $b = 2\kappa_1 - 3\kappa_2\eta_0$, $c = \kappa_4 - 2\kappa_1\eta_0 + 3\kappa_2\eta_0^2$ and η_0 is the solution of the steady-state deterministic equation

$$\kappa_1\eta_0^2 - \kappa_2\eta_0^3 + \kappa_3 - \kappa_4\eta_0 = 0\,. \tag{7.7.161}$$

Here a few remarks are in order. The third-order noise $\zeta(t)$ contributes to $O(V^{-1})$ to the mean and to $O(1)$ to the variance, but contributes to $O(V)$ to the skewness coefficient. If one is only interested in calculating the mean and the variance to $O(V)$, the third-order noise may be dropped from (7.7158) and the expansiou carried out in powers of $\varepsilon = V^{-1/2}$. Also note that as $c \to 0$, the variance and the higher order corrections become divergent. This of, course, is due to the fact that in this limit, the reaction system exhibits a first-order phase transition type behaviour.

8. Spatially Distributed Systems

Reaction diffusion systems are treated in this chapter as a prototype of the host of spatially distributed systems that occur in nature. We introduce the subject heuristically by means of spatially dependent Langevin equations, whose inadequacies are explained. The more satisfactory multivariate master equation description is then introduced, and the spatially dependent Langevin equations formulated as an approximation to this description, based upon a system size expansion. It is also shown how Poisson representation methods can give very similar spatially dependent Langevin equations without requiring any approximation.

We next investigate the consequences of such equations in the spatial and temporal correlation structures which can arise, especially near instability points. The connection between local and global descriptions is then shown. The chapter concludes with a treatment of systems described by a distribution in phase space (i.e. the space of velocity and position). This is done by means of the *Boltzmann Master equation*.

8.1 Background

The concept of space is central to our perception of the world, primarily because well-separated objects do not, in general, have a great deal of influence on each other. This leads to the description of the world, on a macroscopic deterministic level, by *local* quantities such as local density, concentration, temperature, electromagnetic potentials, and so on. Deterministically, these are normally thought of as obeying partial differential equations such as the *Navier-Stokes* equations of hydrodynamics, the *reaction diffusion* equations of chemistry or *Maxwell's* equations of classical electromagnetism.

The simplest cases to consider are reaction diffusion equations, which describe chemical reactions and which form the main topic of this chapter. In order to get some feel of the concept, let us first consider a Langevin equation description for the time evolution of the concentration ρ of a chemical substance. Then the classical reaction-diffusion equation can be derived as follows. A diffusion *current* $\boldsymbol{j}(\boldsymbol{r}, t)$ exists such that

$$\boldsymbol{j}(\boldsymbol{r}, t) = -D\nabla\, \rho(\boldsymbol{r}, t) \tag{8.1.1}$$

and (8.1.1) is called Fick's law. If there is no chemical reaction, this current obeys a conservation equation. For, considering an arbitrary volume V, the total amount of chemical in this volume can only change because of transport across the boundary $\boldsymbol{S}$, of V. Thus, if N is the total amount in V,